

CALORIMETRIC DETERMINATION OF THE
HEATS OF REACTION OF LITHIUM AND
CESIUM WITH THE AMMONIUM ION IN
LIQUID AMMONIA

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Thesis

CALORIMETRIC DETERMINATION OF THE HEATS OF
REACTION OF LITHIUM AND CESIUM WITH THE AMMONIUM ION
IN LIQUID AMMONIA

By

Robert Harris Maybury
(B.S., Eastern Nazarene College, 1944)
submitted in partial fulfilment of the
requirements for the degree of
Master of Arts
1948

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Approved
by

First Reader

Fowell V. Coulter
Professor of Chemistry

Second Reader

Edward O. Holmes, Jr.
Professor of Chemistry

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OUTLINE

CALORIMETRIC DETERMINATION OF THE HEAT OF REACTION OF LITHIUM METAL WITH THE ADDITION 196 IN LIQUID NITROGEN

Page

I. Introduction and Statement of the Problem	1
II. Experimental	5
A. Apparatus	5
1. The Calorimeter	9
2. The Gas-collecting System	11
3. The Electrical Measuring System	12
B. Reagents	14
1. Assembly of the Alkali Metal Samples	15
2. Sample Preparations	15
3. Procedure for Making Calorimetric Determinations	20
III. Presentation of the Data	28
IV. Calculations	30
A. Calculations of the Temperature Change	30
B. Calculations of the Heat Capacity	32
C. Calculation of the Molar Heat Effect	34
Note concerning sample purity correction factor to be applied to lithium heat effects	34
V. Discussion of the Results: Conclusions	41
VI. Abstract	77
VII. Appendix	82
A. Calibration of Thermocouple	83
B. Determination of Heat Capacity of Calorimeter	92
VIII. Classified Bibliography	94

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OUTLINE
CALORIMETRIC DETERMINATION OF THE HEATS OF
REACTION OF LITHIUM AND CESIUM WITH THE AMMONIUM ION IN
LIQUID AMMONIA

	<u>Page</u>
I. Introduction and Statement of the Problem	1
II. Experimental	8
A. Apparatus	8
1. The Calorimeter	9
2. The Gas-collecting System	11
3. The Electrical Measuring Equipment	13
B. Experimental Procedure	14
1. Assembly of the Alkali Metal Samples	15
2. Advance Preparations	19
3. Procedure for Making Calorimetric Determinations	20
III. Presentation of the Data	28
IV. Calculations	50
A. Calculations of the Temperature Change	50
B. Calculations of the Heat Capacity	52
C. Calculation of the Molar Heat Effect	54
Note concerning sample purity correction factor to be applied to Lithium heat effects	56
V. Discussion of the Results. Conclusions	73
VI. Abstract	77
VII. Appendix	83
A. Calibration of Thermocouple	83
B. Determination of Heat Capacity of Calorimeter	92
VIII. Classified Bibliography	98

CHAPTER II
 CALORIMETRIC METHOD OF THE MEASUREMENT OF
 REACTION OF METALS AND ALLOYS WITH AIR AND O₂ IN
 LIQUID MEDIUM

1	I. Introduction and Statement of the Problem
2	II. Experimental
3	A. Apparatus
4	1. The Calorimeter
5	2. The Gas-collecting System
6	3. The Electrical Heating Equipment
7	B. Experimental Procedure
8	1. Assembly of the Alloy Metal Samples
9	2. Sample Preparation
10	3. Procedure for Making Calorimetric Determinations
11	III. Presentation of the Data
12	IV. Calculations
13	A. Calculations of the Temperature Change
14	B. Calculations of the Heat Capacity
15	C. Calculations of the Heat Effect
16	Notes concerning sample purity correction factor to be applied to lithium heat effects
17	V. Discussion of the Results. Conclusions
18	VI. Abstract
19	VII. Appendix
20	A. Calibration of Thermocouples
21	B. Determination of Heat Capacity of Calorimeter
22	VIII. Classified Bibliography

TABLES

<u>Table</u>	<u>Page</u>
1. Typical Analysis of Lithium Metal	16
2. Representative Sizes of Alkali Metal Samples	18
3. Data of Experiment C (Lithium)	30
4. Data of Experiment E (Lithium)	32
5. Data of Experiment F (Lithium)	34
6. Data of Experiment G (Lithium)	37
7. Data of Experiment A (Cesium)	40
8. Data of Experiment C (Cesium)	43
9. Data of the Determination of the Heat of Solution of Lithium	46
10. Data of the Determination of the Heat of Solution of Ammonium Bromide	48
11. Heat Capacity of Liquid Ammonia	53
12. Heat of Vaporization of Liquid Ammonia	54
13. Sample of Calculations of the Heat of Reaction ΔH_1	59
14. Summary of Calculations of Experiment C (Lithium)	63
15. Summary of Calculations of Experiment E (Lithium)	65
16. Summary of Calculations of Experiment F (Lithium)	66
17. Summary of Calculations of Experiment G (Lithium)	67
18. Summary of Calculations of Experiment A (Cesium)	68
19. Summary of Calculations of Experiment C (Cesium)	69
20. Summary of Calculations for the Determination of the Heat of Solution of Lithium	70
21. Summary of Calculations for the Determination of the Heat of Solution of Ammonium Bromide.	71

TABLES

Page	Topic
16	1. Typical Analysis of Lithium Metal
18	2. Gross Active Sites of Alkali Metal Samples
20	3. Data of Experiment C (Lithium)
22	4. Data of Experiment E (Lithium)
24	5. Data of Experiment F (Lithium)
26	6. Data of Experiment G (Lithium)
28	7. Data of Experiment A (Cesium)
30	8. Data of Experiment C (Cesium)
32	9. Data of the Determination of the Heat of Solution of Lithium
34	10. Data of the Determination of the Heat of Solution of Ammonium Bromide
36	11. Heat Capacity of Liquid Ammonia
38	12. Heat of Vaporization of Liquid Ammonia
40	13. Sample of Calculations of the Heat of Reaction ΔH
42	14. Summary of Calculations of Experiment G (Lithium)
44	15. Summary of Calculations of Experiment E (Lithium)
46	16. Summary of Calculations of Experiment F (Lithium)
48	17. Summary of Calculations of Experiment G (Lithium)
50	18. Summary of Calculations of Experiment A (Cesium)
52	19. Summary of Calculations of Experiment C (Cesium)
54	20. Summary of Calculations for the Determination of the Heat of Solution of Lithium
56	21. Summary of Calculations for the Determination of the Heat of Solution of Ammonium Bromide

TABLES

<u>Table</u>	<u>Page</u>
22. Summary of the Experiments	72
23. Heats of Reaction ΔH_3	72a
24. Thermocouple Calibration Data Using Solid Carbon Dioxide	85
25. Summary of Calculations for Thermocouple Calibration using Solid Carbon Dioxide and Mercury	86
26. Calibration Table for Thermocouple TC-1	88
27. Calibration Table for Thermocouple TC-1	89
28. Calibration Table for Thermocouple TC-1	90
29. Comparison of Values of E_{TC-1} Calculated by Three Methods	91
30. A Working Table of Calibration for Thermocouple TC-1	92
31. A Summary of Calorimeter Heat Capacity Determinations	97

Table

Page	Table
72	Summary of the Literature
73	Table of Reaction Data
74	Thermodynamic Data Table
75	Summary of Literature for Thermodynamic Data Table
76	Table of Reaction Data for Thermodynamic Data Table
77	Table of Reaction Data for Thermodynamic Data Table
78	Table of Reaction Data for Thermodynamic Data Table
79	Table of Reaction Data for Thermodynamic Data Table
80	Table of Reaction Data for Thermodynamic Data Table
81	Table of Reaction Data for Thermodynamic Data Table
82	Table of Reaction Data for Thermodynamic Data Table
83	Table of Reaction Data for Thermodynamic Data Table
84	Table of Reaction Data for Thermodynamic Data Table
85	Table of Reaction Data for Thermodynamic Data Table
86	Table of Reaction Data for Thermodynamic Data Table
87	Table of Reaction Data for Thermodynamic Data Table

ILLUSTRATIONS

<u>Figure</u>	<u>To follow page</u>
1. Conductance Curves of Potassium, Sodium and Lithium Solutions in Liquid Ammonia	2
2. Sectional View of the Calorimeter	8
3. Calorimeter and Mounting	8
4. Photograph of the Calorimeter	8
5. The Gas-collecting System	8
6. Electrical Measuring Equipment Circuit Diagram	8
7. Photograph of Complete Equipment	8
8. Sketch of the Current Interrupter	10
9. A. Cesium Sample-bulb Filling Apparatus	16
B. Ammonia Cylinder	16
10. Temperature Patterns for Experiment C, (Lithium)	50
11. Temperature Patterns for Experiment E, (Lithium)	50
12. Temperature Patterns for Experiment F, (Lithium)	50
13. Temperature Patterns for Experiment G, (Lithium)	50
14. Temperature Patterns for Experiment A, (Cesium)	50
15. Temperature Patterns for Experiment C, (Cesium)	50
16. Temperature Pattern for Heat of Solution of Lithium	50
17. Temperature Pattern for Heat of Solution of Ammonium Bromide	50

ILLUSTRATIONS

To follow page

Figure

1	1. General view of the calorimeter	1
2	2. Sectional view of the calorimeter	2
3	3. Detail view of the calorimeter	3
4	4. Photograph of the calorimeter	4
5	5. The gas-collecting system	5
6	6. Electrical measuring instrument circuit diagram	6
7	7. Photograph of complete equipment	7
8	8. Section of the current interrupter	8
9	9. Section of the current interrupter	9
10	10. Temperature patterns for Experiment A	10
11	11. Temperature patterns for Experiment B	11
12	12. Temperature patterns for Experiment C	12
13	13. Temperature patterns for Experiment D	13
14	14. Temperature patterns for Experiment E	14
15	15. Temperature patterns for Experiment F	15
16	16. Temperature patterns for Experiment G	16
17	17. Temperature patterns for Experiment H	17
18	18. Temperature patterns for Experiment I	18
19	19. Temperature patterns for Experiment J	19
20	20. Temperature patterns for Experiment K	20
21	21. Temperature patterns for Experiment L	21
22	22. Temperature patterns for Experiment M	22
23	23. Temperature patterns for Experiment N	23
24	24. Temperature patterns for Experiment O	24
25	25. Temperature patterns for Experiment P	25
26	26. Temperature patterns for Experiment Q	26
27	27. Temperature patterns for Experiment R	27
28	28. Temperature patterns for Experiment S	28
29	29. Temperature patterns for Experiment T	29
30	30. Temperature patterns for Experiment U	30
31	31. Temperature patterns for Experiment V	31
32	32. Temperature patterns for Experiment W	32
33	33. Temperature patterns for Experiment X	33
34	34. Temperature patterns for Experiment Y	34
35	35. Temperature patterns for Experiment Z	35

ILLUSTRATIONS

Figure

To follow page

- | | |
|---|----|
| 18. Comparison of Determinations of the Heat of Solution of Ammonium Bromide | 74 |
| 19. Current Diagram for Determination of the Heat Capacity of the Calorimeter | 92 |
| 20. Heat Capacity of Calorimeter | 95 |

INSTRUCTIONS

to follow page

21012

18. Comparison of watermeter of the last
of solution of ammonia nitrate
74
19. Current meter for determination of the
best capacity of the calorimeter
75
20. Best capacity of calorimeter
76

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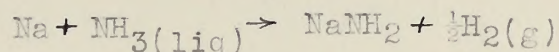
CALORIMETRIC DETERMINATION OF THE HEATS OF REACTION
OF LITHIUM AND CESIUM WITH THE AMMONIUM
ION IN LIQUID AMMONIA

The alkali metals dissolve in liquid ammonia at -33°C to form true solutions of a bronze-like appearance when very concentrated and of a deep blue color when dilute. The solvent ability of liquid ammonia for sodium and potassium metals was observed in 1864 by Weyl¹. Later Moissan² found lithium, cesium, rubidium and calcium metals soluble in ammonia. Quantitative studies by Ruff and Giesel³ reported one gram-atom of sodium, potassium and lithium soluble in 587, 474, and 387 moles of liquid ammonia respectively.

Early qualitative investigations pointed out unusual properties of these solutions. Cady⁴ discovered that liquid ammonia solutions of sodium metal exhibited much greater conductivity than did solutions of sodium salts. Vapor pressure measurements by Kraus^{5c}, who assumed Raoult's Law in the treatment of his data, indicated the apparent molecular weight of sodium in liquid ammonia solutions was less than 23.

1. Weyl, Ann. Physik 121, 601 (1864)
2. Moissan, Compt. Rend. 127, 685 (1898) 128, 26 (1899); 136, 1177 (1903)
3. Ruff and Geisel, Ber. 39, 828 (1906)
4. Cady, J. Phys. Chem. 1, 707 (1897)
5. a. C.A. Kraus, J. Am. Chem. Soc. 29, 1557 (1907)
b. Ibid 30, 653 (1908)
c. Ibid 30, 1197 (1908)
d. Ibid 30, 1323 (1908)
e. Ibid 36, 864 (1914)
f. Ibid 43, 749 (1921)

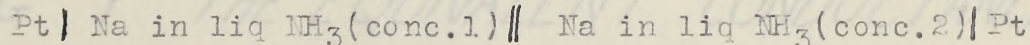
A certain amount of dissociation of sodium was therefore assumed. The sodium-liquid ammonia solutions were found to be quite stable although decomposition with formation of the amide and evolution of hydrogen gas was catalyzed by iron oxide or platinum black:



Phase study diagrams revealed the absence of any irreversible compound formation in the case of the alkali metal solutions^{5b} whereas definite ammoniates of the type $\text{Ca}(\text{NH}_3)_6$, $\text{Sr}(\text{NH}_3)_6$ and $\text{Ba}(\text{NH}_3)_6$ were formed in solutions of the alkaline earth metals.

Careful studies by Kraus^{5e} of the conductivities of alkali metal solutions confirmed the ionic nature of the conduction process. The positive carrier was identified as the positive metal ion. On the other hand, the negatively charged carrier was identified as the same in solutions of different metals. It was postulated to be the electron, free or associated with the solvent. The various properties of the solutions were attributed to the presence of this common negative ion.

From E.M.F. measurements using concentration cells of the type:



Kraus calculated the speed of the negatively charged carrier to be 7 times that of the positively charged carrier in dilute solutions and 280 times as great as the positive carrier in concentrated solutions. Thus the conduction of the current in the concentrated solution is essentially metallic whereas in the

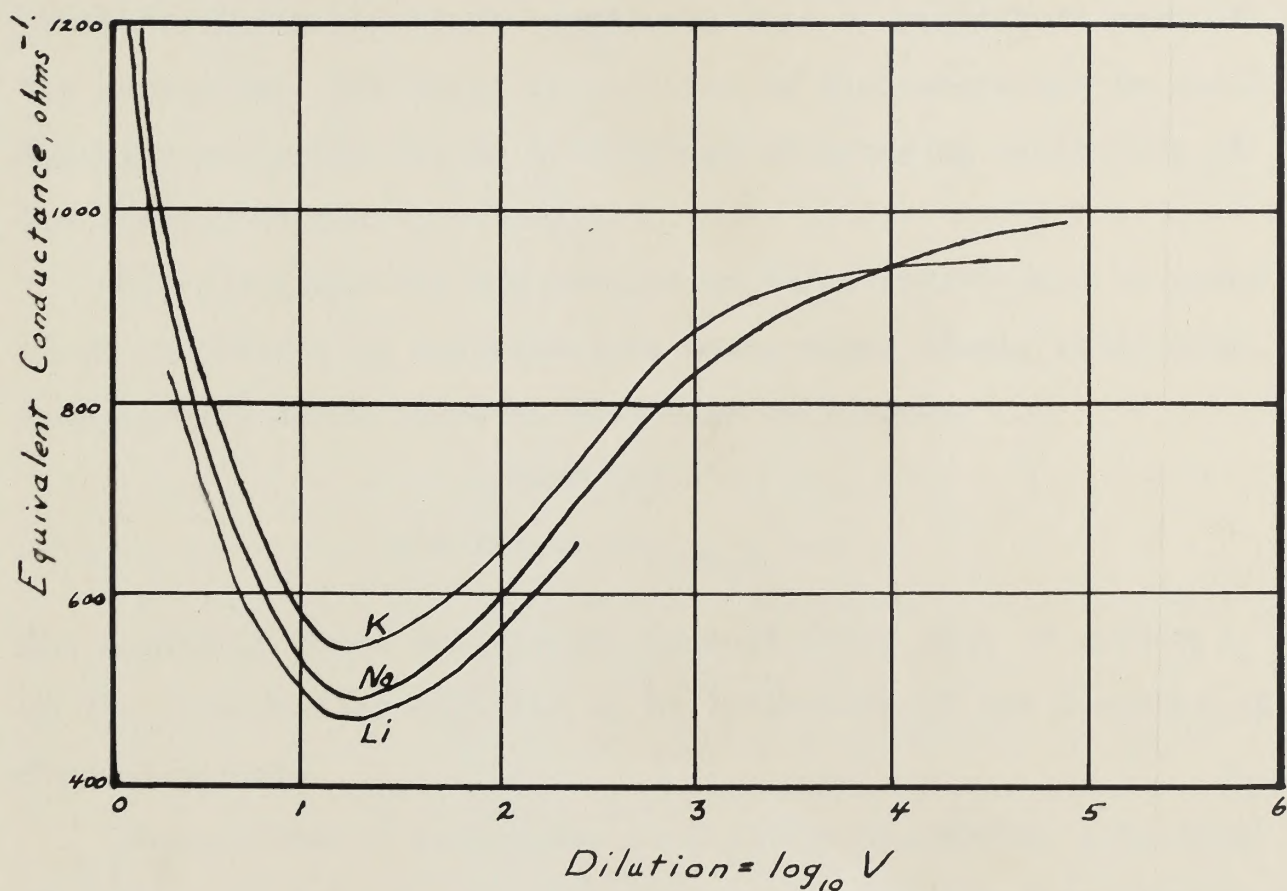


FIG. 1 THE EQUIVALENT CONDUCTANCE OF SOLUTIONS OF ALKALI METALS IN LIQUID AMMONIA AT -33.5°C . V = liters liquid NH_3 / g atom metal.



Graph of $y = \sqrt{x}$ for $0 \leq x \leq 4$

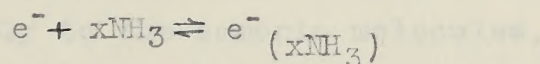
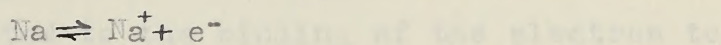
The area under the curve is shaded.

The area is approximately 2.67 square units.

dilute solution, conduction is electrolytic.

Figure 1 shows the conductance curves of potassium, sodium and lithium solutions as measured by Kraus.^{5f} A definite minimum in the curve for each metal is observed at a concentration of 0.05 N. The marked similarity of these curves indicated the presence of the identical negatively charged carrier in each of the solutions. The small differences in the curves may be qualitatively accounted for by differences in carrying capacities of the respective positive ions.

Kraus interpreted the results of these experiments in terms of an equilibria in the solutions among metal atoms, metal ions, free electrons and solvated electrons as follows:



The unusually large conductance (almost twice that of mercury) in the concentrated solution is an indication of the presence of free electrons.

The minimum in each curve as dilution increases, according to Kraus, is caused by increasing solvation of the free electrons. Finally, the rise of the conductance curve towards a limiting value results from continued dissociation of the metal into ions and electrons, largely solvated in the more dilute regions.

Additional evidence of the presence of an identical species in all of the alkali metal solutions was obtained by Gibson and Argo⁶ who observed that the absorption spectra of all of the

6. Gibson and Argo, J. Am. Chem. Soc., 40, 1327 (1918)

solutions were the same at equal concentrations, and were quite different from those of the alkaline earth metal solutions.

Magnetic susceptibility studies⁷ of alkali metal solutions reveal that the concentrated solutions are diamagnetic whereas the dilute are paramagnetic. Theoretical explanations of the diamagnetism vary particularly with respect to the possible equilibria that might be responsible for reducing the contribution of the unpaired electrons to magnetic susceptibility. However, all agree to the presence of single electrons in the dilute solutions. Photoelectric measurements by Hasing⁸ point out that the energy distribution of the electrons in the dilute solution are different from those in the concentrated solution, and this is best attributed to the binding of the electron to some center possibly to the ammonia molecules.

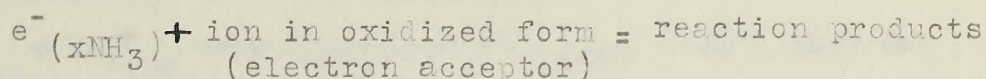
Whereas, the structure to be associated with the solution of an alkali metal has not been determined, the presence of an identical species in the dilute solutions of all the alkali metals is indicated by these conductivity studies, absorption spectra, magnetic susceptibilities and photoelectric measurements.

If such a species is present in all the solutions, it is reasonable to assume that other properties of the solutions could be shown to have a unique dependence on the presence of the common species. The similarity of any such property in all

7. Freed and Thode, Nature, 134, 774 (1934)
 Freed and Sugarman, J.Chem.Phys. 11, 354 (1943)
 Huster, Ann. Physik, 33, 477 (1938)
 Yost and Russell, Systematic Inorganic Chemistry,
 Prentice Hall, N.Y. (1944)
8. Hasing, Ann. Physik, 33, 509 (1940)

the solutions would tend to confirm the existence of the identical species, the solvated electron, in each solution

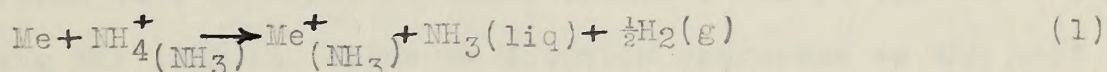
For example, it is to be expected that the heat of reduction of some particular ion in each case by the solvated electron would give the same value, regardless of the metal.



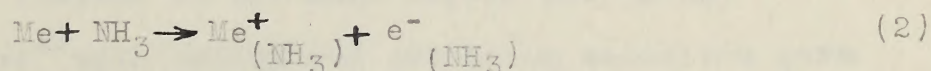
Direct determination of the heat of reduction for this above reaction by measuring the heat evolved upon mixing a liquid ammonia solution of an alkali metal containing the solvated electron with a liquid ammonia solution of an ammonium salt as a source of the ammonium ion, the ion in the oxidized state, is not feasible because of experimental difficulties.

Indirect determination of this heat of reduction may be obtained, however, by the combination of the heat effects associated with two easily studied reactions.

The solid alkali metals react with the ammonium ion in liquid ammonia as follows:⁹



where ΔH_1 is the heat effect accompanying the reaction. This reaction and its corresponding ΔH_1 value may be combined with the reaction representing the solution of the solid alkali metal in pure liquid ammonia,



which has heat effect designated ΔH_2 , to give the desired reaction between the solvated electron and ammonium ion together

⁹. Fernelius and Watt, Chem.Rev., 20, 195 (1937)

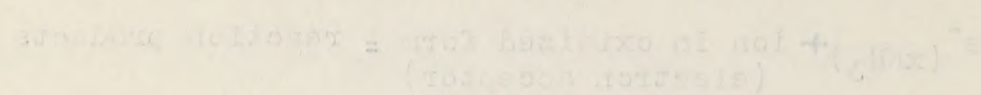
the solution would tend to neutralize the influence of the solvent.

calculated, the solvent effect, in each case.

the example, it is to be expected that the heat of reduction

of some reaction for in each case by the solvent effect

would give the same value, regardless of the solvent.



direct determination of the heat of reduction for this above re-

action by measuring the heat evolved upon mixing a typical amount

the solution of an electrolyte containing the reduced electron

with a typical amount of the electrolyte as a source

of the electrolyte ion, the ion in the oxidized state, is not res-

able because of experimental difficulties.

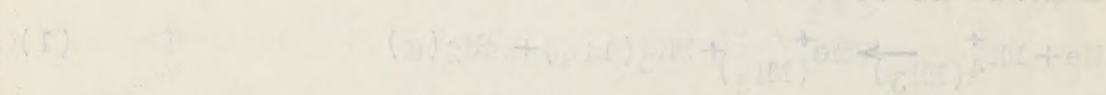
Indirect determination of this heat of reduction may be

obtained, however, by the combination of the heat effects meas-

ured with two easily studied reactions.

The solid state heat of reaction with the electrolyte ion in

the solution is as follows:

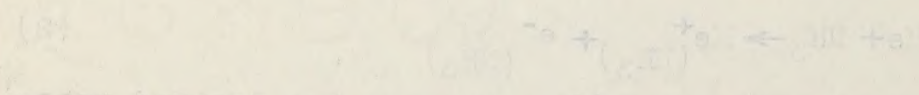


where ΔH_f° is the heat effect accompanying the reaction. This

reaction and its corresponding ΔH_f° value may be compared with

the reaction representing the solution of the solid state

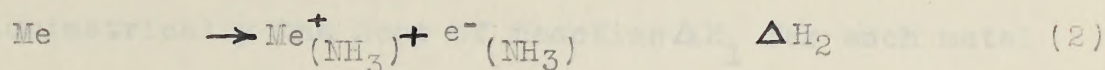
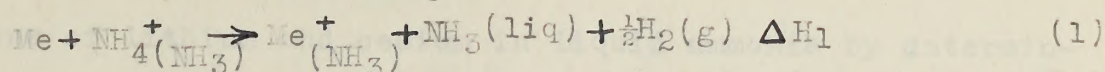
in pure liquid ammonia:



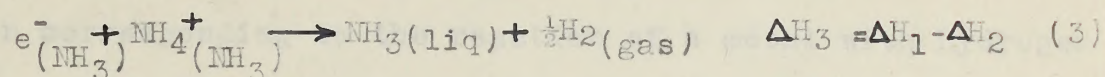
which has heat effect ΔH_{sol}° , to give the desired reac-

tion between the reduced electron and electrolyte ion together

with its heat of reaction, ΔH_3 , as follows:



subtracting (2) from (1) and rearranging



Equation (3), then, represents a specific reaction involving the reduction of the ammonium ion which should possess a heat of reaction, ΔH_3 , independent of the alkali metal used.

This present research consists of the measurement of the heat of reaction, ΔH_1 , of equation 1 which then has been combined with a value of ΔH_2 obtained from the literature to give a calculated value for ΔH_3 .

Actual determinations of the heat of reaction are made with solutions of finite concentration whereas values for the infinitely dilute solution are those required. By finding the heat of reaction as a function of concentration, one is justified in accepting the limiting value as dilution increases as the heat of reaction for the infinitely dilute solutions. The heats of solution found in the literature must also be obtained for the infinitely dilute region by a similar assumption regarding the limiting values reached in the more dilute solutions.

Initial work¹⁰ with sodium and potassium solutions gave indications of a constant heat of reaction ΔH_3 . The purpose of

10. Unpublished research by L.V. Coulter

the present research has been to extend the measurements to solutions of lithium and cesium in liquid ammonia by determining calorimetrically the heat of reaction ΔH_1 for each metal with the ammonium ion. At the same time, additional thermodynamic data in the liquid ammonia system has been gathered for a reaction corresponding to the reaction of a metal with hydrogen ion in aqueous solution. Also, the information obtained concerning the nature of the alkali metal solutions serves as a relative basis upon which a study of the alkaline earth metal solutions may be built. The absorption spectra measurements by Gibson and Argo⁶ have indicated a dissimilarity between alkali and alkaline earth metal solutions. It will be of interest to study the energetics of the system for comparative reasons.

A determination of the heat of solution of lithium to give a very dilute solution yielded a value that differed significantly from the corresponding value found by Schmidt. To uncover any inherent disagreement attributable either to method or apparatus between calorimetric values determined by Schmidt and those determined in this present investigation, a determination of the heat of solution of ammonium bromide was also undertaken. The resulting value agreed sufficiently well with that of Schmidt, thus discounting the possibility of any significant inherent errors.

6. G. A. Argo and A. P. Niederhiser, J. Am. Chem. Soc., 56, 99 (1934)

7. Argo and Niederhiser, 1934, 56, 99 (1934)

8. Argo and Schmidt, 1934, 56, 2397 (1934)

9. Sch. 110, Abstracted by Kluge, J. Am. Chem. Soc., 57, 2799 (1935)

10. Schmidt, Zander and Poltyshin, 1934, 56, 2780 (1934)

the present research has been to extend the measurements to solutions of lithium and sodium in liquid ammonia by determining the calorimetric heat of reaction ΔH_1 for each metal with the ammonia ion. At the same time, additional thermodynamic data in the liquid ammonia system has been gathered for a reaction corresponding to the reaction of a metal with hydrogen ion in aqueous solution. Also, the formation of solvated ions in the nature of the alkali metal solutions serves as a relative basis upon which a study of the alkaline earth metal solutions may be built. The absorption spectra measurements by Gibson and Argo⁵ have indicated a dissimilarity between alkali and alkaline earth metal solutions. It will be of interest to study the energetics of the system for comparative reasons.

A determination of the heat of solution of lithium to give a very dilute solution yielded a value that differed slightly from the corresponding value found by Schmidt. To uncover any inherent disagreement attributable either to method or apparatus between calorimetric values determined by Schmidt and those determined in this present investigation, a determination of the heat of solution of ammonia bromide was also undertaken. The resulting value agreed sufficiently well with that of Schmidt, thus discounting the possibility of any significant inherent errors.

II. Experimental

The calorimetric determination of ΔH_1 consists of measurement of the heat effect produced in the course of reaction (1). The alkali metal is allowed to react with the ammonium salt in liquid ammonia and the resulting temperature change of the solution and calorimeter is measured. The gases evolved during the reaction, hydrogen and vaporized solvent, are collected in a gas-collecting system of known volume. The heat of the reaction is then calculated from the temperature change of the calorimeter and contents and from the heat effect associated with the ammonia vaporized.

Apparatus

The properties of liquid ammonia necessitate special apparatus and techniques in its use in quantitative procedures. Special techniques for making thermochemical studies in the liquid ammonia system have been developed by Kraus^{5,11} and Schmidt.¹² The apparatus used in this research was essentially as described by Schmidt with certain modifications. In place of the absorption bulb for the evolved ammonia, a gas-collecting vessel was used. A much larger calorimeter was used which had a volume of 200 ml as compared with 30 ml for the volume of the calorimeter used by Schmidt, thus facilitating investigation in the more dilute regions.

11. a. C.A. Kraus and J.⁴. Ridderhof, J. Am. Chem. Soc. 56, 79 (1934)

b. Kraus and Prescott, ibid, 56, 86 (1934)

c. Kraus and Schmidt, ibid, 56, 2297 (1934)

12. a. Schmidt, Sottysiak and Kluge, J. Am. Chem. Soc. 58, 2509 (1936)

b. Schmidt, Studer and Sottysiak, ibid, 60, 2780 (1938)

1. Experimental

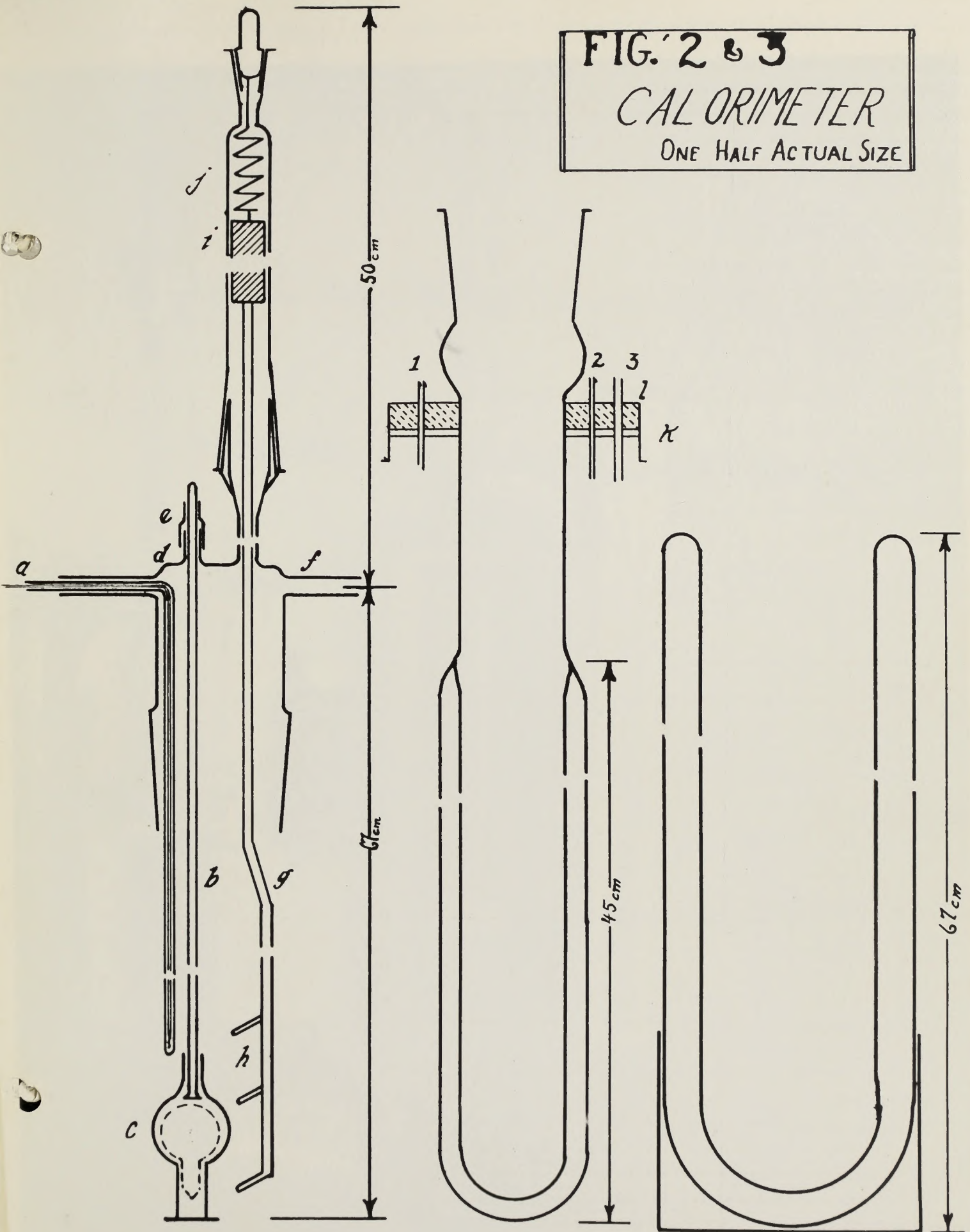
The calorimetric determination of ΔH consists of measurement of the heat effect produced in the course of reaction (1). The alkali metal is allowed to react with the ammonia salt in liquid ammonia and the resulting temperature change of the solution and calorimeter is measured. The gases evolved during the reaction, hydrogen and various solvents, are collected in a gas-collecting system of known volume. The heat of the reaction is then calculated from the temperature change of the calorimeter and contacts and from the heat effect associated with the ammonia vaporized.

Apparatus

The properties of liquid ammonia necessitate special apparatus and techniques in its use in quantitative procedures. Special techniques for making thermochemical studies in the liquid ammonia system have been developed by Evans, Schmidt, and Schmidt. The apparatus used in this research was essentially as described by Schmidt with certain modifications. In place of the absorption bulb for the evolved ammonia, a gas-collecting vessel was used. A much larger calorimeter was used which had a volume of 100 ml as compared with 50 ml for the volume of the calorimeter used by Schmidt. This facilitating investigation in the more definite regions.

11. G. A. Evans and J. A. Schmidt, *J. Am. Chem. Soc.*, **56**, 79 (1934).
12. G. A. Evans and J. A. Schmidt, *ibid.*, **56**, 85 (1934).
13. G. A. Evans and J. A. Schmidt, *ibid.*, **56**, 2237 (1934).
14. G. A. Schmidt, *ibid.*, **56**, 2237 (1934).
15. G. A. Schmidt, *ibid.*, **56**, 2237 (1934).
16. G. A. Schmidt, *ibid.*, **56**, 2237 (1934).

FIG. 2 & 3
CALORIMETER
 ONE HALF ACTUAL SIZE



HEAD PORTION

INNER DEWAR

OUTER DEWAR

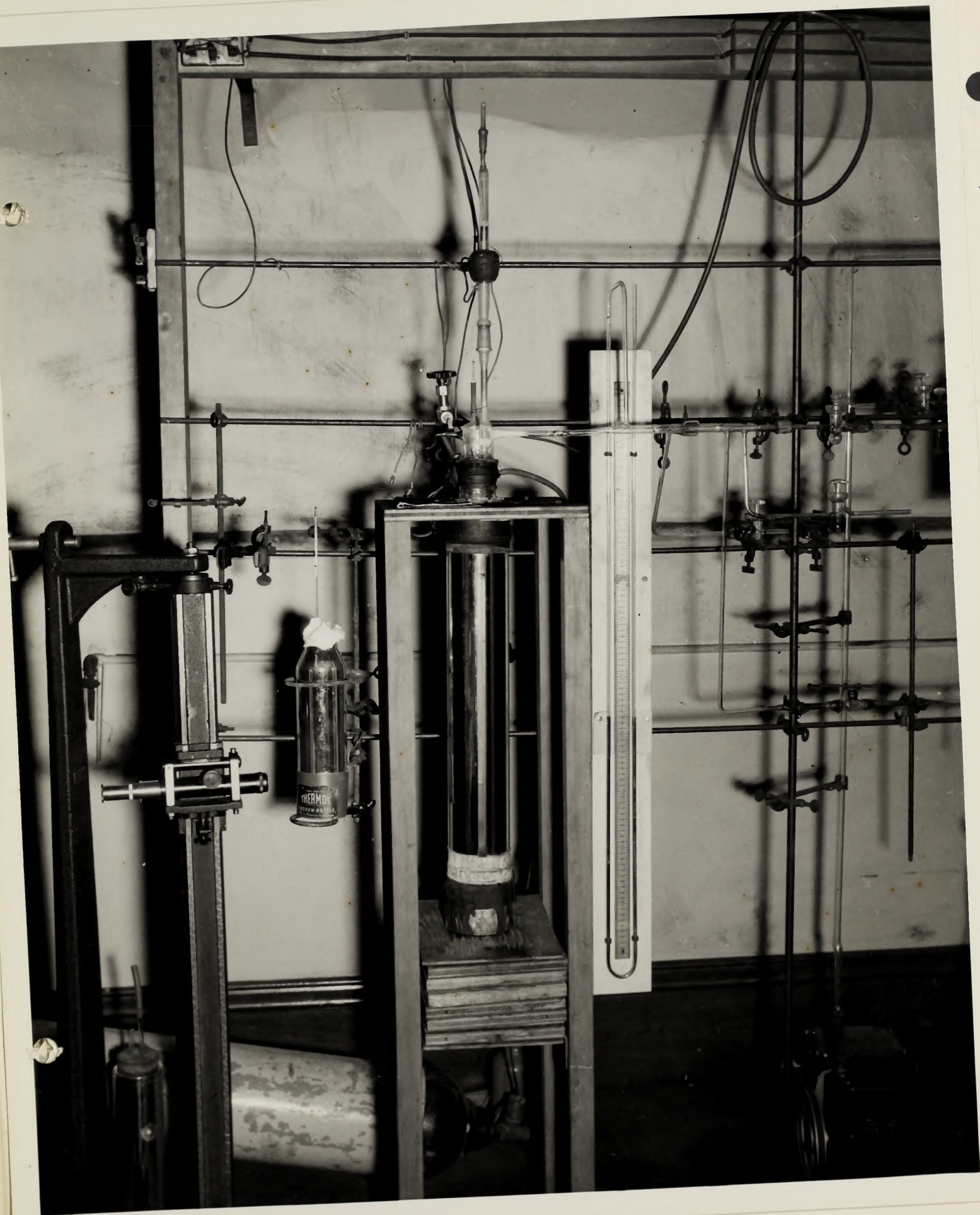




FIG. 5

GAS COLLECTING SYSTEM

NOT DRAWN TO SCALE

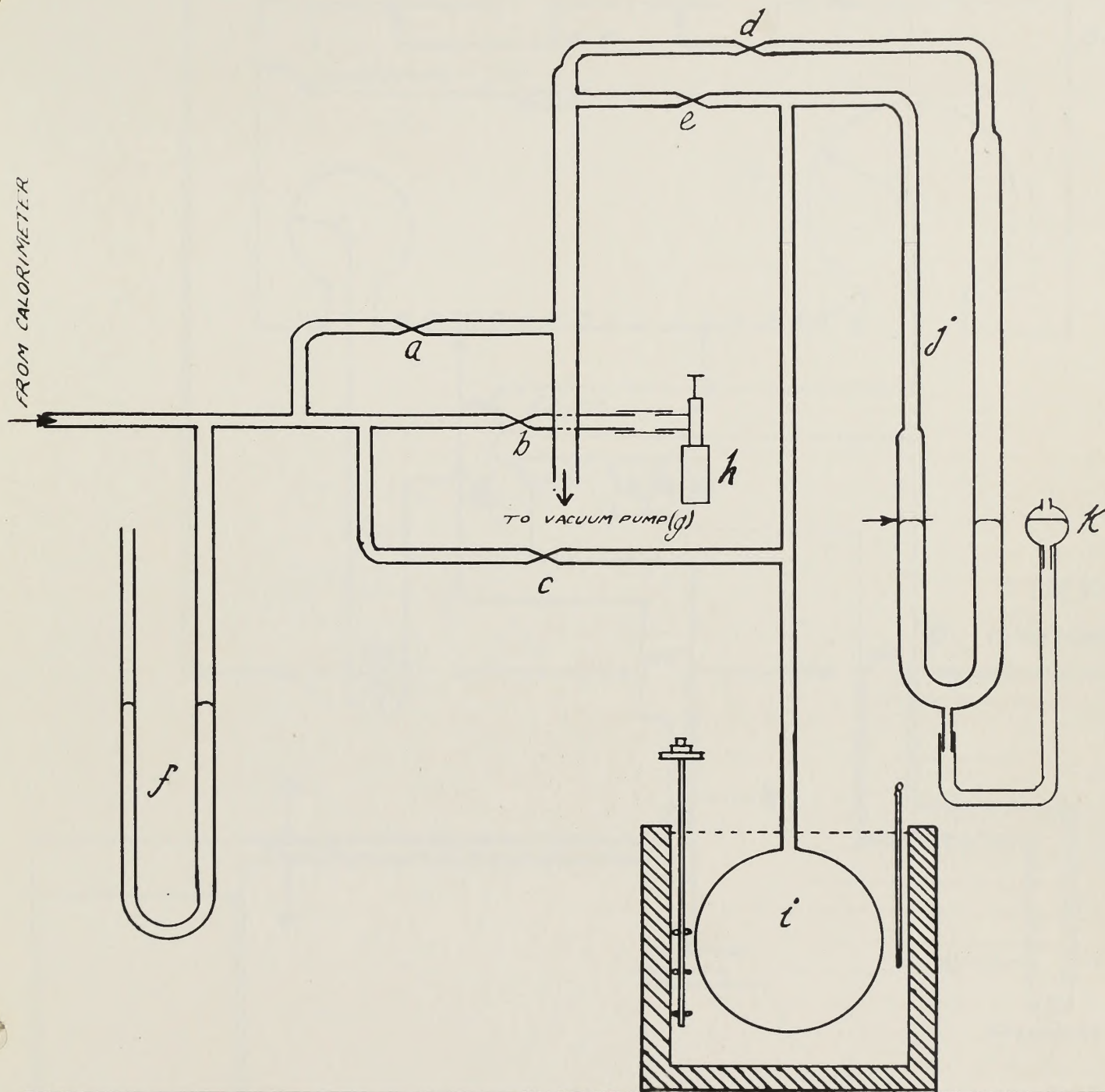


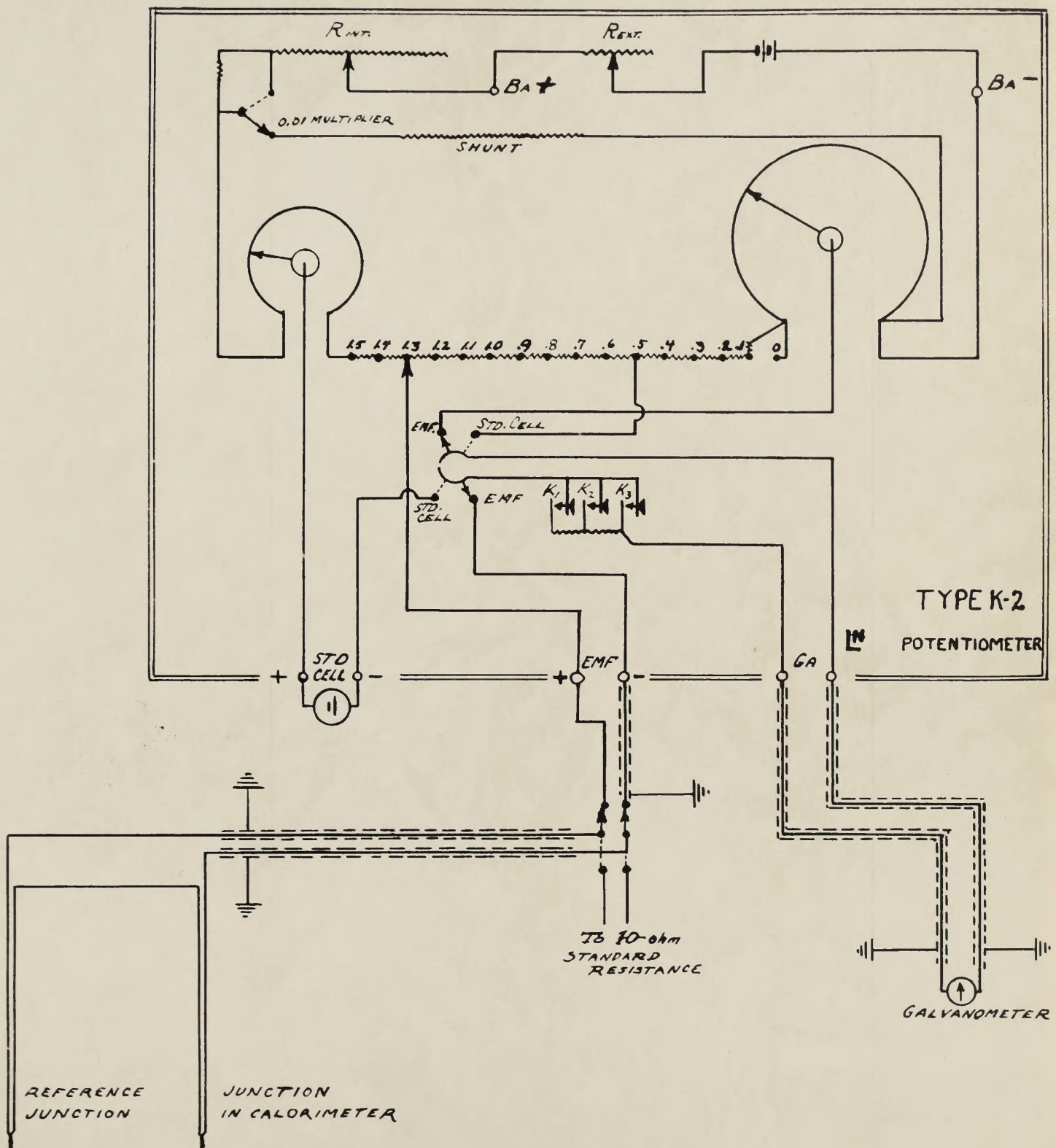
FIG. 2
PLAN OF THE SYSTEM
OF THE

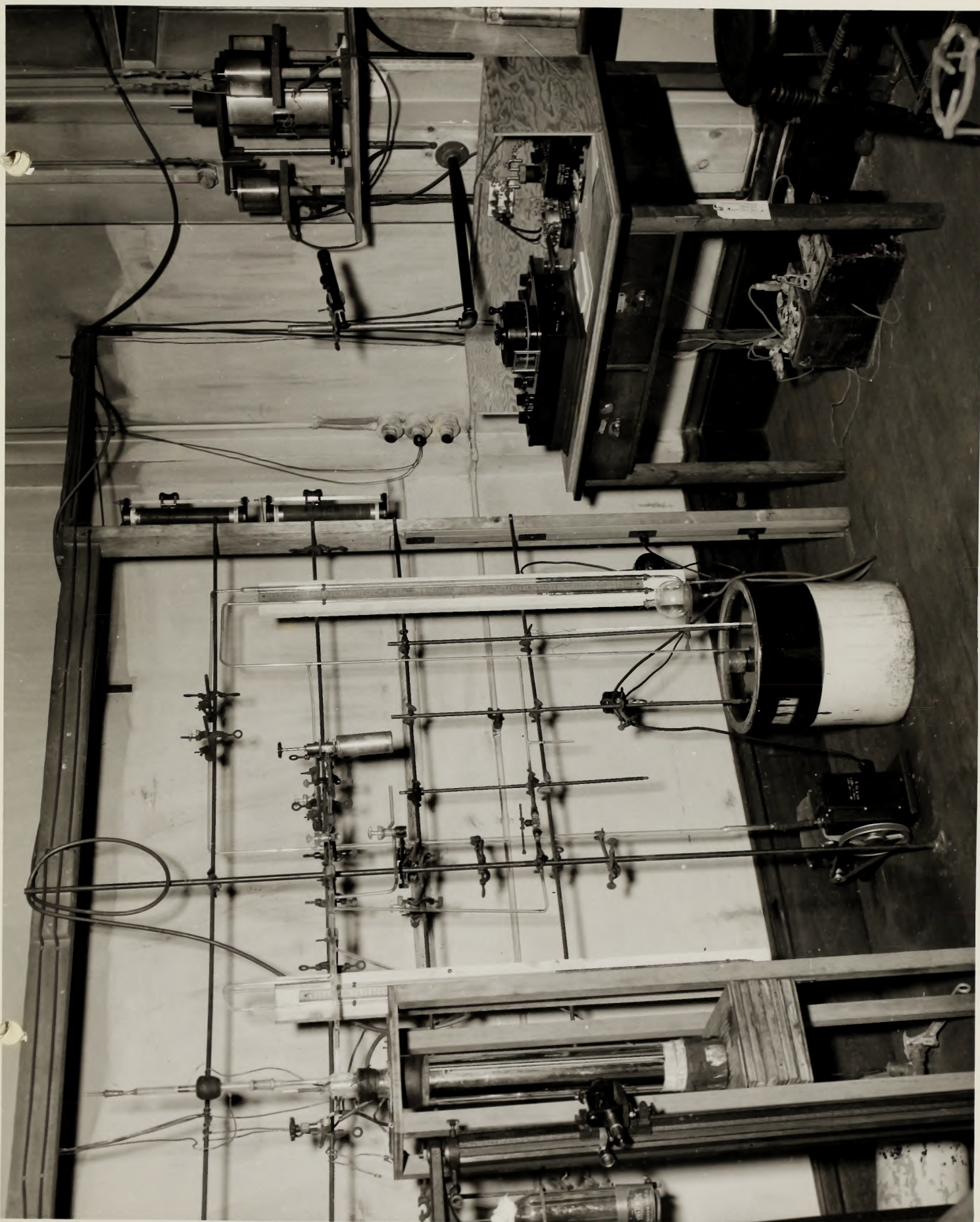


FIG. 6

ELECTRICAL MEASURING EQUIPMENT

SIMPLIFIED WIRING DIAGRAM (NOT DRAWN TO SCALE)





The apparatus consists of the following parts:

1. The calorimeter (Figures 2,3 and 4)
2. The gas-collecting system (Figures 5 and 7)
3. The electrical measuring equipment (Figures 6&7)

1. The calorimeter consists of an inner jacket or Dewar vessel outside diameter 6 cm, outside length 45 cm, fitted with a head portion by means of a ground glass joint, standard taper 55/50. Surrounding this inner Dewar is a large outer Dewar 10 cm. outside diameter and 67 cm. outside length.

The inner Dewar is constructed as illustrated in figure 2, the double thickness walls comprising the lower two thirds of the overall length. The single walled ring seal above these joins to the ground glass joint. The inner Dewar is held in place in a wooden stand by a close fitting collar around the upper part of the ring seal. (See Figure 3). The underside of this collar is covered with a thick rubber gasket which forms a gas tight seal with the lip of the large outer Dewar when the latter is raised up around the inner Dewar. Three inlet tubes extend through the collar and gasket into the space between the two Dewars. To one of the inlet tubes, inlet tube 1, is attached a length of rubber tubing that extends to the outside bottom of the inner Dewar. To the second of the inlets, inlet tube 2, a short length of rubber tubing is attached. The third inlet tube, inlet tube 3, connects with the out-of-doors for the purpose of venting the outer Dewar.

Both inner and outer Dewars have an unsilvered vertical band a centimeter in width at the front and back to permit

The apparatus consists of the following parts:

1. The calorimeter (Figures 2, 3 and 4)
 2. The gas-collecting system (Figures 5 and 7)
 3. The electrical measuring equipment (Figures 6, 7)
1. The calorimeter consists of an inner jacket or Dewar vessel outside diameter 8 cm, outside length 45 cm, fitted with a hand portion by means of a ground glass joint, standard taper 35/50. Surrounding this inner Dewar is a large outer Dewar 10 cm outside diameter and 57 cm outside length.

The inner Dewar is constructed as illustrated in Figure 2. The double thickness walls comprising the lower two thirds of the overall length. The single walled ring seal above these joins to the ground glass joint. The inner Dewar is held in place in a wooden stand by a close fitting collar around the upper part of the ring seal. (See Figure 3). The underside of this collar is covered with a thick rubber gasket which forms a gas tight seal with the lip of the large outer Dewar when the latter is raised up around the inner Dewar. Three inlet tubes extend through the collar and gasket into the space between the two Dewars. To one of the inlet tubes, inlet tube 1, is attached a length of rubber tubing that extends to the outside bottom of the inner Dewar. To the second of the inlets, inlet tube 2, a short length of rubber tubing is attached. The third inlet tube, inlet tube 3, connects with the out-of-doors for the purpose of venting the outer Dewar.

Both inner and outer Dewars have an unslanted vertical

band a centimeter in width at the front and back to serve

observation of the contents of the vessels.

The head is held securely in place by a small spring stretched across the top. The head portion fitted to the inner Dewar contains the thermocouple junction, the sample-bulb rod and the stirrer. The thermocouple junction and leads are contained in a well (a) made of 3 mm. glass tubing. A small amount of naphthalene at the bottom of the thermocouple well provides increased heat conductivity accelerating the response of the junction to temperature changes. The well is sealed into the head portion by means of a beeswax-rosin mixture which is unaffected by the vapors of ammonia.

The sample-bulb rod (b) is constructed of 3 mm. tubing and extends to a point near the bottom of the inner Dewar. At its lower end is attached a platinum stirrup (c) to hold the fragile sample-bulb. The sample-bulb rod enters the head portion by a guide (d) 1.8 cm. in length and 4 cm. in diameter that is sealed to the head portion. A 2 cm. length of rubber tubing slipped over both the end of the guide and over the protruding end of the sample-bulb rod is wired to both in such a manner as to make a gas tight connection, but so that a few millimeters play is allowed the rod.

The stirrer (g) that extends into the inner Dewar also is a length of 3 mm. tubing to which at points near the lower end are attached glass paddles (h) 1 cm. in diameter which effect agitation of the liquid when moved in short vertical strokes of 3 cm. in length. The upper part of the stirring rod is attached to a

Observation of the contents of the vessels.

The head is held securely in place by a small spring clip at across the top. The head portion is fitted to the inner lower contains the thermocouple junction. The sample-rod rod and the stirrer. The thermocouple junction and leads are connected in a well (a) made of 3 mm. glass tubing. A small amount of nitrogen gas at the bottom of the thermocouple well provides increased heat conductivity accelerating the response of the junction to temperature changes. The well is sealed into the head portion by means of a beeswax-resin mixture which is unaffected by the vapors of ammonia.

The sample-rod rod (b) is constructed of 3 mm. tubing and extends to a point near the bottom of the inner Dewar. At its lower end is attached a platinum stirrer (c) to hold the fragile sample-rod. The sample-rod rod enters the head portion by a guide (d) 1.8 cm in length and 4 mm in diameter that is sealed to the head portion. A 2 cm length of rubber tubing slipped over each end of the guide and over the protruding end of the sample-rod rod is wired to both in such a manner as to make a gas tight connection, but so that a few millimeters play is allowed the rod.

The stirrer (e) also extends into the inner Dewar also is a length of 3 mm. tubing to which at points near the lower end are attached glass paddles (f) 1 cm in diameter which effect agitation of the liquid when moved in about vertical strokes of 2 cm in length. The upper part of the stirring rod is attached to a

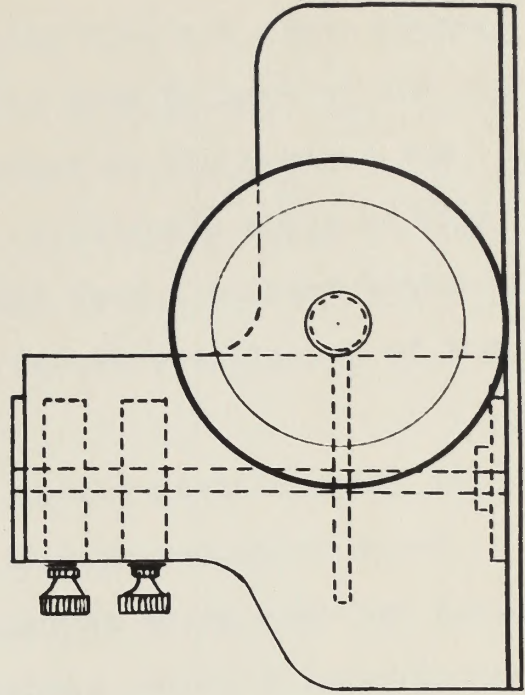
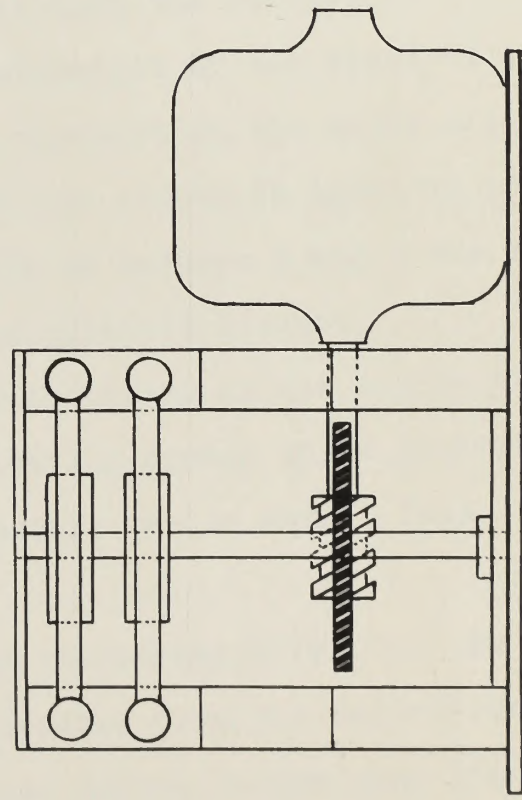
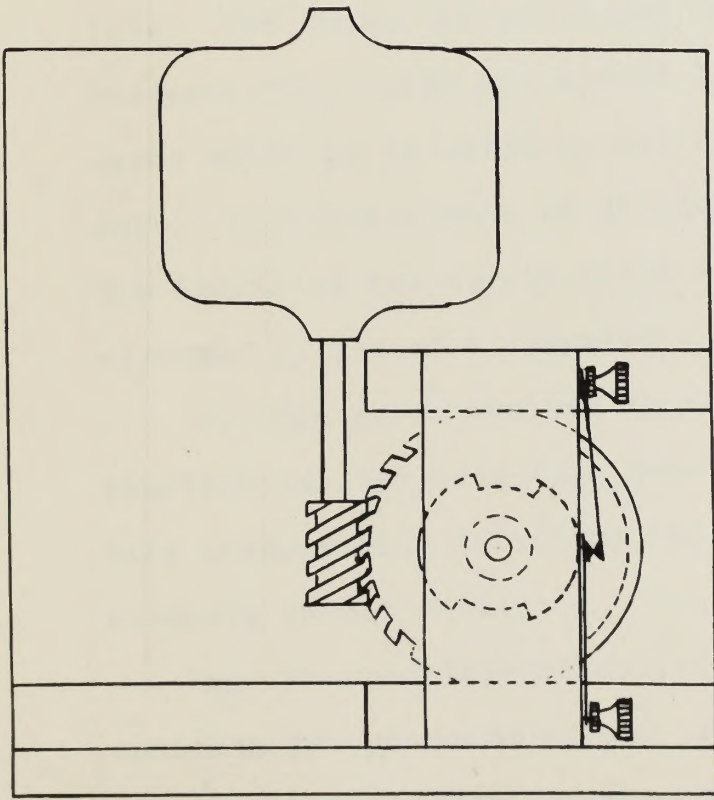


FIG 8 CURRENT INTERRUPTER
SIMPLIFIED SKETCH - 1/3 SIZE



soft iron cylinder (i) that is suspended within a glass sleeve by a spring (j). The metal cylinder is free to move up and down inside the glass sleeve which is attached to the head of the calorimeter by a ground glass joint. A solenoid slips on over the glass sleeve. Intermittent current from a current interrupter when passed through the solenoid causes oscillation of the iron cylinder.

The construction of the current interrupter is shown in figure 8. A 1/20 hp motor 1725 rpm through reduction gears turns the series of slotted discs, against which rest two spring steel extensions carrying contact points. Circuit interruption results when the disks are rotated allowing the extensions with contact points attached to spring back into the slots at intervals. The number of times per minute that the circuit is successively closed and opened is determined by the speed of the motor which is adjusted by use of a rheostat in the motor circuit. A stirring rate of 60 strokes per minute is commonly used. The length of the stroke which should be between 3 and 4 cms. is adjusted by use of a rheostat in the solenoid circuit.

2. The gases evolved in the calorimeter in the course of a reaction are led over to a gas-collecting system where quantitative measurements of volume and pressure may be made. This assembly consists of:

- a. An open-type mercury-filled manometer (Fig. 5-f) to indicate the pressure in the line leading from the calorimeter.
- b. A line that leads to a motor driven vacuum pump (Cenco Hyvac) (g). This line can be closed off by means of a mercury

soft iron cylinder (1) that is suspended within a glass sleeve by a spring (2). The metal cylinder is free to move up and down inside the glass sleeve which is attached to the head of the calorimeter by a round glass joint. A solenoid coil is connected to the glass sleeve. Intermittent current from a current interrupter when passed through the solenoid causes oscillation of the iron cylinder.

The construction of the current interrupter is shown in Figure 1. A 1/20 hp motor 1725 rpm through reduction gears turns the series of slotted discs, a shaft which has two spring steel extensions carrying contact points. Current interruption results when the discs are rotated allowing the extensions with contact points attached to spring back into the slots at intervals. The number of times per minute that the circuit is successively closed and opened is determined by the speed of the motor which is adjusted by use of a rheostat in the motor circuit. A striking rate of 60 strokes per minute is commonly used. The length of the stroke which should be between 3 and 4 cms is adjusted by use of a rheostat in the solenoid circuit.

2. The gases evolved in the calorimeter in the course of a reaction are led over to a gas-collecting system where quantitative measurements of volume and pressure may be made. This

assembly consists of:

- a. An open-type mercury-filled manometer (Fig. 2-1) to indicate the pressure in the line leading from the calorimeter.
- b. A line that leads to a motor driven vacuum pump (Genco Model 2). This line can be closed off by means of a mercury

seal ground glass stopcock. (a)

C. A thermostated vessel (i), 6715 ml. capacity, for collecting gases. The gas-collecting vessel is outfitted with a closed-type manometer (j), constructed of 14 mm. tubing which reduces surface tension effects on the meniscus for indicating the pressure of the enclosed gases. In the line that leads to this vessel from the calorimeter is located a needle-valve (c) for controlling the rate at which gases may be drawn off from the reacting materials in the calorimeter. The needle valve of metal construction is connected to the glass line by use of the beeswax-rosin compound. The gas-collecting vessel is immersed in a large water bath along with a small electric stirrer and a thermometer. This system is maintained at 25°C when gas measurements are made. The closed type manometer is constructed so that the right arm may be evacuated through the stopcock. The left arm opens into the gas-collecting vessel. The mercury level in the two arms may be adjusted by raising or lowering a mercury reservoir (k) connected at the bottom of the manometer.

d. A short line shut off by a mercury seal vacuum stopcock (b). This line serves as a convenient place for an attachment of the steel cylinder (h) (See also Fig. 9B) filled with liquid ammonia for transfer to the calorimeter. The cylinder (h) 23cm. over all length, 5 cm. in diameter through the containing body, holds about 115 grams of anhydrous liquid ammonia and is equipped with a needle valve to regulate the flow of ammonia vapor into the evacuated calorimeter. The valve and the metal joints of

steel ground glass stopcock. (a)
C. A thermostated vessel (1) 575 ml capacity, for collecting
the gas. The gas-collecting vessel is outfitted with a closed
type manometer (2), constructed of 14 mm. tubing which reduces
surface tension effects on the manometer for indicating the pres-
sure of the enclosed space. In the line that leads to this
vessel from the calorimeter is located a needle-valve (c) for
controlling the rate at which gases may be drawn off from the
receiving materials in the calorimeter. The needle valve of
metal construction is connected to the glass line by use of the
beeswax-rosin compound. The gas-collecting vessel is immersed
in a large water bath along with a small electric stirrer and a
thermometer. This system is maintained at 25°C when gas measure-
ments are made. The closed type manometer is constructed so
that the right arm may be evacuated through the stopcock. The
left arm opens into the gas-collecting vessel. The mercury level
in the two arms may be adjusted by raising or lowering a mercury
reservoir (3) connected at the bottom of the manometer.
d. A short line shut off by a mercury seal vacuum stopcock
(4). This line serves as a convenient place for an attachment
of the steel cylinder (5) (See also fig. 3b) filled with liquid
ammonia for transfer to the calorimeter. The cylinder (5) 25 cm.
over all length, 5 cm. in diameter through the containing body,
holds about 15 grams of anhydrous liquid ammonia and is equipped
with a needle valve to regulate the flow of ammonia vapor into
the evacuated calorimeter. The valve and the metal joints of

the cylinder contain packing to eliminate any leakage of ammonia gas.

3. The calorimetric method used to measure the heats of reaction necessitates regular observations of the temperature of the calorimeter through a long period of time. High precision and convenience dictate the use of a thermocouple for these measurements.

The electrical measuring equipment (Fig.6) to execute these measurements consists of a single copper-constantan thermocouple (a and b of Fig. 6) (the calibration of this thermocouple is described in the appendix), a type K-2 Leeds and Northrup potentiometer (c), a Leeds and Northrup galvanometer, Cat.#2500 matched for the circuit (sensitivity 0.35 uv/mm, external critical damping resistance of 55 ohms, a period of 6 seconds, and resistance of 11.4 ohms) and an Eppley Laboratory standard cell, (e) (1.01880 volts) as certified by Eppley Laboratories.

The galvanometer is mounted in a Julius Suspension, Leeds and Northrup Cat. No. 2162. A meter scale suspended from the ceiling of the laboratory ten feet from the floor and at a distance of ten feet from the galvanometer is reflected by the mirror of the galvanometer into a 10 power telescope provided with a vertical crosshair and mounted immediately in front of the observer seated before the potentiometer. Such an arrangement provides a sensitivity of 1.5 scale divisions (mm). per microvolt.

The galvanometer is enclosed in a cylindrical copper shield which is grounded along with shields of the galvanometer and thermocouple leads.

the cylinder contain packing to eliminate any leakage of ammonia gas.

3. The calorimetric method used to measure the heat of reaction necessitates regular observations of the temperature of the calorimeter through a long period of time. This is avoided and convenience dictates the use of a thermocouple for these measurements.

The electrical measuring equipment (Fig. 6) to excite these thermocouples consists of a circuit in copper-constantan thermocouple leads (a & b of Fig. 6) (the calibration of this thermocouple is described in the appendix), a type K-2 Leeds and Northrup potentiometer (c), a Leeds and Northrup galvanometer, Cat. 49500 matched for the circuit (sensitivity 0.55 $\mu\text{V/mm}$, external circuit resistance of 55 ohms, a period of 6 seconds, and resistance of 11.4 ohms) and an Appleby Laboratory standard cell (e) (1.01830 volts) as certified by NBS.

The galvanometer is mounted in a Julius Engelke lead shield and Northrup Cat. No. 2162. A meter scale suspended from the ceiling of the laboratory ten feet from the floor and at a distance of ten feet from the galvanometer is reflected by the mirror of the galvanometer into a 10 power telescope provided with a vertical crosshair and mounted immediately in front of the observer seated before the potentiometer. Such an arrangement provides a sensitivity of 1.5 scale divisions per microvolt. The galvanometer is enclosed in a cylindrical copper shield which is protected along with shields of the galvanometer and thermocouple leads.

Two storage batteries are connected to the potentiometer circuit through an external resistance of 5 ohms through the coarse and fine resistances in the potentiometer. This circuit remains closed at all times to provide an even discharge rate of the batteries.

The reference junction of the thermocouple, located near the calorimeter, is immersed in a small Dewar filled with crushed ice and water.

B. Experimental Procedure

The molar heat of reaction of an alkali metal with the ammonium ion is measured by observing the change in temperature of the reacting and containing system and by observing the volume of the ammonia gas evolved during the reaction.

The temperature of the calorimeter and contents is measured at one minute intervals through a period that precedes the start of the reaction, through the period in which reaction is occurring and through a rating period which follows completion of the reaction. Observation of a continuous constant rate of temperature change for five to ten minutes comprises the anterior period. The reaction is then initiated by crushing the bulb containing the alkali metal sample. The gases evolved in the course of the reaction are collected in the gas-collecting vessel where observation of the resulting pressure permits quantitative determination of their amounts.

Preparations for the experiment include assembly of the

The charge battery is connected to the potentiometer circuit through an external resistance of 5 ohms. The potentiometer and the resistance in the potentiometer. This circuit remains closed at all times to provide an even discharge rate of the battery.

The reference junction of the thermocouple, I rated near the calorimeter, is immersed in a small beaker filled with crushed ice and water.

5. Experimental procedure

The total heat of reaction of an alkali metal with the ammonium ion is observed by observing the change in temperature of the reaction. A constant system and by observing the volume of the ammonia gas evolved during the reaction.

The temperature of the calorimeter and contents is measured at one minute intervals through a period that precedes the start of the reaction, through the period in which reaction is occurring and through a rising period which follows completion of the reaction. Observation of a continuous constant rate of temperature change for five to ten minutes comprises the reaction period. The reaction is then initiated by crushing the bulb containing the alkali metal sample. The gases evolved in the course of the reaction are collected in the gas-collecting vessel where observation of the resulting pressure permits quantitative determination of their amounts.

Preparations for the experiment include assembly of the

calorimeter and adjustment of the electrical measuring equipment.

1. Assembly of the alkali metal samples

a. The alkali metal to take part in a reaction is contained in a small fragile glass bulb, on the end of the sample-bulb rod and is immersed in the liquid ammonia in the calorimeter. The fragile bulb is made from a length of 6 mm. pyrex glass tubing, the end of which is rapidly fused together in the oxygen-gas flame of the hand torch and quickly blown out to a thin-walled bulb of 10 to 12 mm. diameter. The thin bulb should yield without breaking to the light pressure of a pencil point pressed against it and should not collapse when evacuated.

The volume, to the nearest hundredth of a milliliter, of the bulb part is determined by filling with water from a graduated pipette.

The stem is cut off to the required length and fire polished. If the fragile bulb is to contain lithium metal, a close-fitting length of glass rod is provided to fill the entire stem section which is made 6 cm. long. Experience indicated the necessity of using this rod to fill up the stem section, for otherwise unreacted alkali metal tended to accumulate in this recess. If the bulb is to contain cesium metal, the stem near the bulb is constricted to capillary size and in addition, a standard taper (5/20) male joint is sealed to the upper end of the stem.

The completed bulb is cleaned, dried and weighed along with the glass rod, if used, to the nearest tenth of a milligram.

calorimeter and adjustment of the electric measuring equipment.

1. Assembly of the alkali metal samples

a. The alkali metal to take part in a reaction is contained in a small fragile glass bulb, on the end of the bulb a thin rod is inserted in the liquid ammonia in the calorimeter. The fragile bulb is made from a length of 6 mm. glass tubing, the end of which is rapidly fused together in the oxygen-lamp flame of the hand torch and quickly blown out to a thin-walled bulb of 10 to 12 mm. diameter. The thin bulb should yield without cracking to the light pressure of a pencil point pressed against it and should not collapse when evacuated.

The volume, to the nearest hundredth of a milliliter, of the bulb part is determined by filling with water from a graduated pipette.

The stem is cut off to the required length and fire polished. If the fragile bulb is to contain lithium metal, a closing fitting length of glass rod is provided to fill the entire stem section which is made 3 cm. long. Experience indicated the necessity of using this rod to fill up the stem section, for otherwise unreacted alkali metal tended to accumulate in this recess. If the bulb is to contain cesium metal, the stem near the bulb is constructed to resemble a T-joint and in addition a standard taper (3/32) male joint is sealed to the upper end of

the stem.

The completed bulb is cleaned, dried and weighed along with the glass rod, if used, to the nearest tenth of a milligram.

After

b. Lithium: Ingot metallic lithium, purchased from the Lithalloys Corporation, having the following typical analysis was used.

TABLE I

TYPICAL ANALYSIS GIVEN BY LITHALLOYS CORPORATION
FOR THEIR LOW-SODIUM LITHIUM METAL

N	.15%	Ca	.10%
Si	.05	Na	.15
Fe	.02	K	.05
Al	.01		

Cylinders of this material were cut under mineral oil from a block about 1" x 1" x $\frac{1}{2}$ " by a brass corkborer (3 mm. inside diameter). A brass rod fitting the inside of the cork-borer very closely and lubricated with mineral oil, was used to push out the cylinder of lithium metal. With a sharp knife the oxide coating is cut from the top and bottom of the cylinder under oil. The cylinder is then rapidly transferred through a series of three dried benzene washes contained in separate small beakers and thrust into the open stem end of the fragile bulb which is filled with dried benzene and is inverted in a container of the same material. The glass rod is inserted into the stem and aids in directing the lithium metal into the bulb. The bulb is removed from the benzene bath and immediately slipped on the end of a length of rubber tubing that is attached to a vacuum line through a dry ice and acetone trap.

When the bulb has been completely evacuated, a small oxygen gas flame is played around the lower end of the stem near the bulb until the wall collapses onto the glass rod inside the stem. The heating is then increased to effect complete sealing off of

12
 b. Lithium: Lithium metal is obtained from the
 Lithium Corporation, having the following typical analysis
 was used.

TABLE I
 TYPICAL ANALYSIS GIVEN BY LITHIUM CORPORATION
 FOR 99.9% LITHIUM METAL

Li	99.95	Ca	0.10
Na	0.05	Mg	0.15
K	0.05		0.05
Al	0.01		

Cylinders of this material were cut under mineral oil from
 a block about 1" x 1" x 1" by a brass corner (3 mm. inside
 diameter). A brass rod fitting the inside of the corner-
 very closely and lubricated with mineral oil, was used to push
 out the cylinder of lithium metal. With a sharp knife the oxide
 coating is cut from the top and bottom of the cylinder under oil.
 The cylinder is then rapidly transferred through a series of
 three dried benzene washes contained in separate small beakers
 and thrust into the open stem end of the fragile bulb which is
 filled with dried benzene and is inverted in a container of the
 same material. The glass rod is inserted into the stem and side
 in directing the lithium metal into the bulb. The bulb is re-
 moved from the benzene bath and immediately wiped on the end of
 a length of rubber tubing that is attached to a vacuum line
 through a dry ice and acetone trap.
 When the bulb has been completely evacuated, a small oxygen
 gas flame is played around the lower end of the stem near the
 bulb until the wall collapses onto the glass rod inside the stem.
 The heating is then increased to effect complete sealing off of

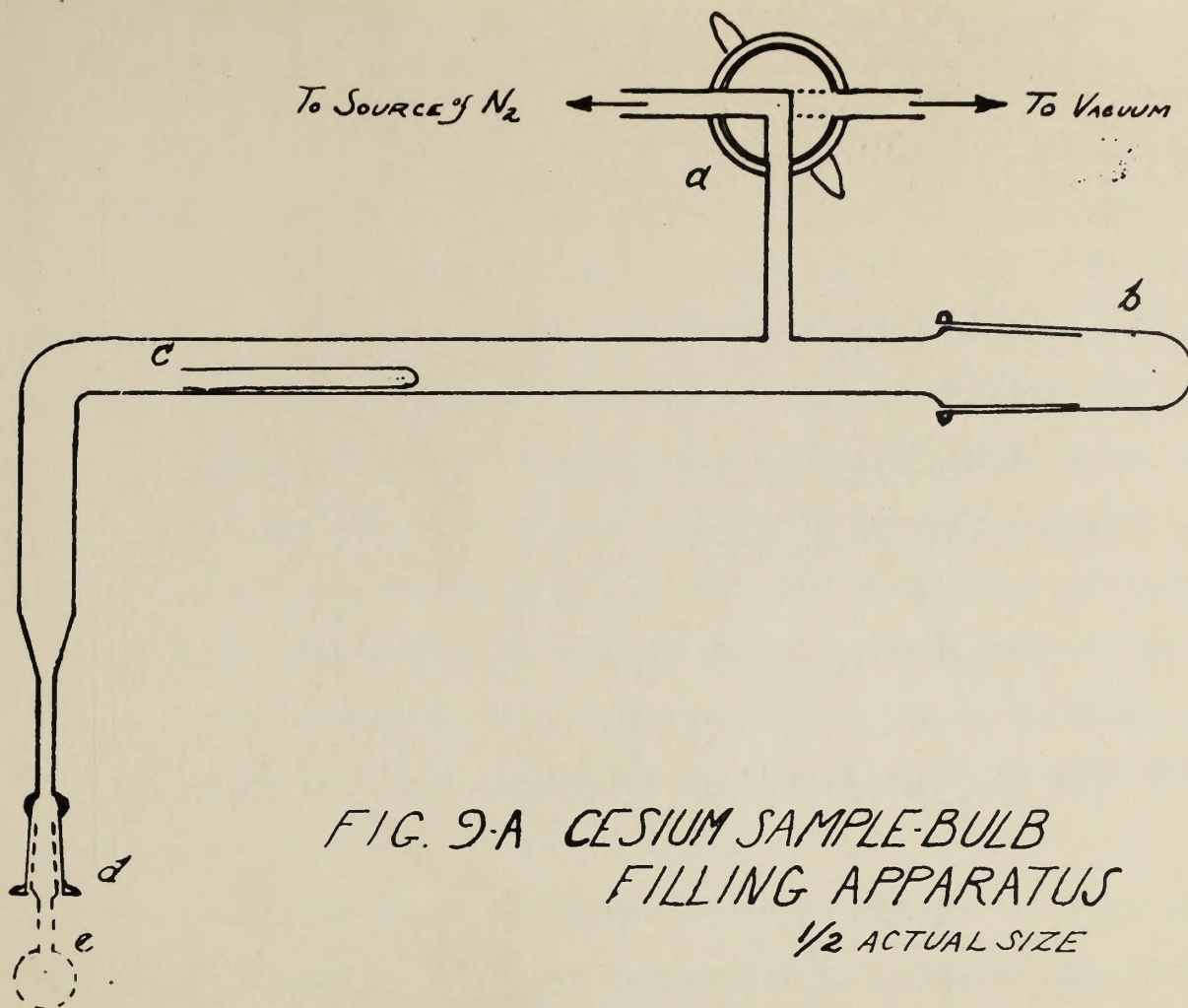


FIG. 9-A CESIUM SAMPLE-BULB
FILLING APPARATUS
1/2 ACTUAL SIZE

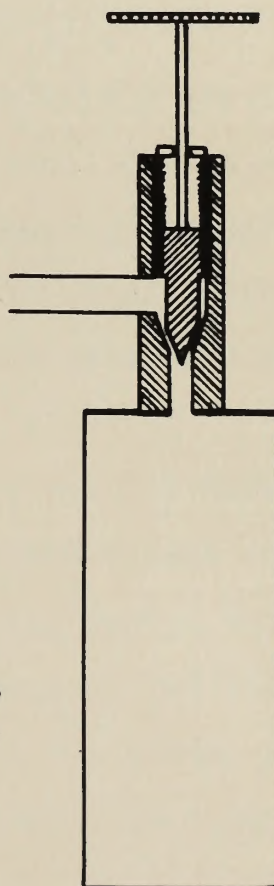


FIG. 9-B: AMMONIA CYLINDER
1/2 ACTUAL SIZE

the bulb at this point. After cooling the bulb is cleaned, dried and weighed. The stem above the seal is removed and the portion remaining on the filled bulb is rounded or pointed to fit the platinum stirrup on the end of the sample-bulb rod.

c. Cesium: Special apparatus for handling cesium metal is shown in figure 9A. The cesium metal used in this research was purchased from Fairmount Chemical Co. as C.P. chemical. The metal was received in thick walled glass tubes sealed off at both ends. Great caution in breaking these ampoules is necessary, for the metal will burn violently if allowed contact with the atmosphere.

The apparatus shown in figure 9A is attached to a high-vacuum line. Stopcock (a) makes connection with either the vacuum line or with a source of nitrogen gas.

The weighed fragile bulb with the ground glass joint (e) is inserted in this apparatus at (d). A small amount of stopcock lubricant is carefully applied to the male joint grinding at the end farthest removed from the opening to avoid later contamination of the cesium in the bulb by melted lubricant flowing down inside the stem.

An oil bath surrounding the fragile bulb is necessary for two reasons. Heating the oil prevents the molten cesium metal from solidifying in the stem constriction during the filling process. More important, should fracture of the bulb occur in any way, the oil bath serves to protect the molten cesium metal from exposure to the air which would result in a serious fire.

the pump at this point. After cooling the bulb is cleared, dried and weighed. The glass above the seal is removed and the portion remaining on the filled bulb is removed or retained to fill the plastic tubing on the end of the sample-bulb rod.

c. Caution: Special attention for handling cesium metal is shown in Figure 2A. The cesium metal used in this research was purchased from Richmond Chemical Co. as 99.9% chemical. The metal was received in a black waxed glass tube sealed off at both ends. Great caution in breaking these ampoules is necessary. For the metal with bare violently it allowed contact with the atmosphere.

The apparatus shown in Figure 2A is attached to a high-vacuum line. Stopcock (a) makes connection with either the vacuum line or with a source of nitrogen gas.

The weighed fragile bulb with the ground glass joint (a) is inserted in this apparatus at (b). A small amount of stopcock lubricant is carefully applied to the male joint grinding at the end of the cesium in the bulb by melted lubricant flowing down inside the stem.

An oil bath surrounding the fragile bulb is necessary for two reasons. First, the oil prevents the molten cesium metal from solidifying in the stem constriction during the filling process. More important, should fracture of the bulb occur in any way, the oil bath serves to protect the molten cesium metal from exposure to the air which would result in a serious fire.

Completely assembled, with sample-bulb in place, the apparatus is ready to operate. It is first completely evacuated and then filled with nitrogen gas. The cap (b) is removed to allow the nitrogen to sweep through the apparatus. A good steady stream should be felt at the opening at (b). An ampoule of cesium is scratched with a file near one end and held in a horizontal position at the opening at (b). The end of the ampoule is broken off with a pair of long-nose pliers and the ampoule thrust into the apparatus at once and pushed to the position at (c). Cap (b) is replaced and the system is evacuated. A small flame from the hand torch is directed around the apparatus near the closed end of the ampoules. The flame is swept along toward the vertical part of the apparatus. By continued combination of these two operations the cesium is vaporized from the ampoule and condensed in the vertical part of the apparatus where collected condensate drops down into the sample-bulb. When all the cesium has been transferred in this manner, the oil bath around the sample-bulb is lowered and the bulb is sealed off at the constriction. It is cleaned, dried and weighed, after which the excess stem and ground glass joint are removed.

Following the above procedures, samples of lithium and cesium were prepared ranging over the sizes described below.

TABLE II
REPRESENTATIVE SIZES OF ALKALI
METAL SAMPLES
Lithium samples Cesium samples

0.0426 g	1.1843 g
0.0321 g	0.7766 g
0.0166 g	
0.0172 g	

Completely assembled, with sample-ship in place, the apparatus is ready to operate. It is first completely evacuated and then filled with nitrogen gas. The cap (b) is removed to allow the nitrogen to sweep through the apparatus. A good steady stream should be felt at the opening at (c). An amount of cesium is scratched with a file near the end and held in a horizontal position at the opening at (b). The end of the capsule is broken off with a pair of long-nose pliers and the sample thrust into the apparatus at once and pushed to the position at (c). Cap (b) is replaced and the system is evacuated. A small flame from the hand torch is directed toward the apparatus near the closed end of the capsule. The flame is swept along toward the vertical part of the apparatus. By continued combustion of these two operations the cesium is vaporized from the capsule and condensed in the vertical part of the apparatus where collected. Condensate drops down into the sample-bulb. When all the cesium has been transferred in this manner, the cap (b) is removed and the sample-bulb is lowered and the bulb is sealed off at the connection. It is cleaned, dried and weighed, after which the excess steel and ground glass joint are removed.

Following the above procedures, samples of lithium and cesium were prepared in the manner over the sizes described below.

TABLE II
ANALYTICAL DATA OF LITHIUM
AND CESIUM SAMPLES

0.0425 g	0.0425 g
0.0421 g	0.0421 g
0.0422 g	0.0422 g
0.0423 g	0.0423 g

2. Advance Preparation for Making the Calorimetric Determinations.

Several hours before and preferably the day preceeding a determination certain preliminary preparations, including cleaning and assembling the calorimeter, are made.

The liquid ammonia used in this research was purchased in steel cylinders containing 100 lbs of ammonia from the Matheson Company and analyzed by them to be 99.7% ammonia with 0.1% nitrogen and 0.2% moisture as impurities.

Ammonia from the large cylinder is condensed in a medium-sized steel cylinder containing metallic sodium which unites with any moisture present. This transfer of ammonia is accomplished by surrounding the medium-sized cylinder with an ice and water bath while the large cylinder is at room temperature. A quarter-inch copper tubing fitted with brass couplings is conveniently used to connect the cylinders. Several hours distillation fills the medium-sized cylinder with a sufficient quantity of ammonia. The small cylinder (h) with needle valve is fitted with copper tubing and coupling by soldering the tubing to the steel sidearm of the cylinder and connection for the purpose of removing any air from the line connecting the two cylinders. Transfer of the ammonia is accomplished by immersing the small cylinder in crushed ice while the medium-sized cylinder is splashed with warm water to hasten the distillation. Generally an hour is sufficient time to fill the small cylinder. At the end of this time, the needle valve is closed and the coupling is disconnected. A rapid approximate weighing of the small cylinder

2. Advance Preparation for Making the Determination

General Notes

Several hours before and preferably the day preceding a determination certain preliminary operations, including cleaning and assembling the colorimeter, are made.

The first ammonia used in this method was obtained in steel cylinders containing 10 lbs of ammonia from the National Gas Company and analyzed by them to be 99.75% ammonia with 0.1% nitrogen and 0.25% moisture as impurities.

Ammonia from the large cylinder is condensed in a medium-sized steel cylinder containing metallic sodium which unites with any moisture present. This transfer of ammonia is accomplished by decomposing the medium-sized cylinder with an ice and water bath while the large cylinder is at room temperature. A water-filled copper tubing fitted with brass couplings is conventionally used to connect the cylinders. Several hours distillation fills the medium-sized cylinder with a sufficient quantity of ammonia. The small cylinder (B) with needle valve is fitted with copper tubing and coupling by soldering the tubing to the steel sidearm of the cylinder and connection for the purpose of removing any air from the line connecting the two cylinders.

Transfer of the ammonia is accomplished by immersing the small cylinder in crushed ice while the medium-sized cylinder is agitated with water to hasten the distillation. Generally ammonia is sufficient time to fill the small cylinder. At the end of this time, the needle valve is closed and the coupling is disconnected. A rapid approximate weighing of the small cylinder

with attached tubing and coupling serves to indicate the amount of ammonia in the cylinder. This amount should not exceed 115 grams. If too much ammonia has been condensed, immediate release of the excess is important to avoid bursting of the cylinder as the contents warm to room temperature. The copper tubing is removed, the solder cleaned off well, and the cylinder and contents weighed to the nearest milligram.

Other preparations made a day ahead of time include cleaning of the calorimeter and checking the operation of the stirrer. The calorimeter is cleaned by using Calgon cleaning solution and a long bristle brush. The cleaning solution is withdrawn by a long glass tube dipping down into the calorimeter and attached to a water aspirator. This cleaning is followed with several rinses of fresh water. Rinses of alcohol or acetone hasten final drying.

The solenoid actuated stirring mechanism is best checked by placing the head portion of the calorimeter into position at the top of the calorimeter. The solenoid is slipped on over the glass sleeve and connected to the source of current from the interrupter. The rheostats are adjusted to obtain the desired strength and period of the intermittent current.

Finally, the battery circuit in the potentiometer is balanced against the standard cell by adjusting the external resistance in the potentiometer to stabilize the battery current.

3. Procedure for Making Calorimetric Determinations

Upon completion of the foregoing preparations, the process of assembling the calorimeter and filling it with liquid ammonia

also attached to the end of the cylinder and connected to the end of the cylinder. This should not exceed 115 mm. If too much ammonia has been condensed, immediate release of the excess is important to avoid bursting of the cylinder as the contents vary to room temperature. The copper tubing is removed, the solder cleaned off well, and the cylinder and contents weighed to the nearest milligram.

Other precautions made a day ahead of time include cleaning of the calorimeter and checking the operation of the stirrer. The calorimeter is cleaned by using Gorton cleaning solution and a long bristle brush. The cleaning solution is withdrawn by a funnel. These steps are done into the calorimeter and stirred as a water aspirator. This cleaning is followed with several rinses of fresh water. Rinses of alcohol or acetone-water final rinses.

The alcohol and water stirred until the solution is best checked by finding the head portion of the calorimeter into position at the top of the calorimeter. The alcohol is slipped on over the glass sleeve and connected to the source of current from the stirrer. The rheostat are adjusted to obtain the desired current and period of the intermittent current.

Finally, the battery circuit in the potometer is balanced against the standard cell by adjusting the external resistance in the potometer to stabilize the battery current.

2. Procedure for Making Calorimetric Determinations

Upon completion of the foregoing preparations, the process of assembling the calorimeter and filling it with liquid ammonia

is commenced. This procedure is followed by the actual determination of the heat of reaction.

Assembly of the calorimeter consists of introducing the desired weight of ammonium salt, inserting the sample-bulb into the platinum stirrup at the lower end of the sample-bulb rod, seating the head portion in the inner Dewar and connecting the calorimeter to the gas-collecting system.

The fragile sample-bulb is placed securely in the platinum stirrup in such a way that the short stem section of the bulb points downward and lodges the bulb firmly in the stirrup. This keeps the bulb in direct line of the thrust of the rod when the rod is pushed downward to crush the bulb. A platinum gauze is wrapped around the bulb to control the rate of the reaction. A suitable number of enlarged holes in the gauze regulates the rate of escape of the entrapped hydrogen evolved as the alkali metal reacts thereby controlling the degree of contact of solution and sample and hence the reaction rate.

With the ground glass surfaces well coated with vacuum sealing compound, the head portion is seated in the calorimeter. The sample bulb rod which has been raised considerably through the guide in the head portion, is adjusted so that the stirrup and bulb rest against the inner bottom of the calorimeter while the end of the rod rests lightly on the gauze covering the fragile bulb. The rubber tubing that slips over the guide and around the protruding sample-bulb rod is now tightly wired to both in a way that will permit movement of the rod through a vertical distance of a centimeter or more.

is connected. This procedure is followed by the actual determination of the heat of reaction.

Assembly of the calorimeter consists of introducing the heated weight of reactant into the reaction cell, inserting the sample-rod into the reaction cell at the lower end of the sample-rod, and sealing the head portion in the inner cover and connecting the calorimeter to the gas-collecting system.

The flexible sample-rod is placed axially in the platinum stirrer in such a way that the short stem section of the bulb points downward and lodges the bulb firmly in the stirrer. This keeps the bulb in direct line of the thrust of the rod when the rod is pushed downward to crush the bulb. A platinum gauze is wrapped around the bulb to control the rate of the reaction. A small number of enlarged holes in the gauze regulates the rate of escape of the evolved hydrogen evolved as the small metal reacts there, controlling the degree of contact of solution and sample and hence the reaction rate.

With the stand glass surface well coated with vacuum sealing compound, the head portion is sealed in the calorimeter. The sample-rod which has been dried considerably through the guide in the head portion, is adjusted so that the stirring and only rest against the inner bottom of the calorimeter while the end of the rod rests lightly on the glass covering the flexible bulb. The rubber tubing that slips over the guide bar around the rotating sample-rod is now tightly wired to both in a way that will permit movement of the rod through a vertical distance of a centimeter or more.

The calorimeter is connected to the gas-collecting system by sealing together the glass line between them. The entire system is then evacuated and returned to atmospheric pressure. This serves to seat the calorimeter head more firmly but produces some strain in the glass connection made above which is removed by heating the tubing to redness and allowing to cool. The system is again evacuated and tested for leaks with a spark coil. The manometers in both the calorimeter line and the gas-collecting system should indicate a constancy in the vacuum over a period of ten or fifteen minutes.

The calorimeter is filled with the dried liquid ammonia contained in the metal cylinder which is attached to the line as shown in figure 5 (h) using tightly wired rubber tubing. The needle valve between the calorimeter and gas-collecting vessel is closed and the calorimeter and line leading from the cylinder is evacuated after which the stopcock between the calorimeter line and the vacuum pump is closed.

The needle valve of the cylinder is opened and distillation of the ammonia from the metal cylinder to the calorimeter is accomplished by surrounding the inner jacket with a freezing mixture of dry ice and acetone or trichloroethylene contained in the large Dewar. The pressure in the line is not permitted to exceed atmospheric by more than sixty millimeters of mercury as indicated by the manometer. The distillation proceeds most rapidly when the freezing mixture is in direct contact with the ring seal of the inner jacket which is of a single thickness of glass permitting rapid heat transfer. The distillation is com-

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plete when the pressure indicated by the manometer suddenly drops to less than atmospheric. The stopcock and needle valve are closed at once and the Dewar containing the freezing mixture is lowered from around the calorimeter. The cylinder is removed and weighed. The difference between its weight when full and this weight is the weight of ammonia transferred to the calorimeter.

In quick succession the outer Dewar is emptied, cleaned, and dried and the outer surface of the calorimeter cleaned and dried in a stream of compressed air. The previously mentioned lengths of rubber tubing are connected to the inlet tubes 1 and 2 of figure 3. Inlet tube 1 is connected through a valve to the liquid ammonia supply from the manufacturer's cylinder. Inlet tube 2 is clamped shut. The outer Dewar is raised up around the calorimeter with the vertical unsilvered areas aligned and firmly pressed against the rubber gasket making a gas tight seal. The outer Dewar is supported in this position with wooden blocks slipped beneath its base.

Liquid ammonia from the cylinder is allowed to flow into the outer Dewar filling the space between it and the calorimeter.

While the outer Dewar is being filled with ammonia, warming of the ammonia in the calorimeter results in some vaporization which causes an increase in the line pressure indicated by the manometer. A pressure of below sixty millimeters in excess of atmospheric is maintained by allowing part of the ammonia vapors to pass over into the previously evacuated gas-collecting vessel.

After the pressure indicator of the manometer and only after
the flow has been started. The stopcock and valve are
closed at once and the Dewar containing the freezing mixture is
lowered down around the calorimeter. The cylinder is removed
and washed. The distance between the weight and bulb and
this weight is the weight of ammonia transferred to the calorimeter.

In quick succession the outer Dewar is emptied, cleaned,
and dried and the outer surface of the calorimeter cleaned and
dried in a stream of compressed air. The previously mentioned
length of rubber tubing now connected to the inlet tube 1 and
to the outer Dewar is connected through a valve to the
inlet ammonia supply from the manufacturer's cylinder. Inlet
tube 2 is changed over. The outer Dewar is raised up around the
calorimeter with the vertical receiver attached and filled
by passing against the rubber gasket with a hand pump. The
outer Dewar is connected in this position with water blocks.

After the outer Dewar is filled with water.
Liquid ammonia from the cylinder is allowed to flow into
the outer Dewar filling the space between it and the calorimeter.
While the outer Dewar is being filled with ammonia, warming
of the ammonia in the calorimeter results in some vaporization
which causes an increase in the line pressure indicated by the
manometer. A pressure of below sixty millimeters in excess of
atmospheric is maintained by allowing part of the ammonia vapors
to pass over into the previously evacuated gas-collecting vessel.

The total amount of ammonia collected in this way is calculated from the pressure of the gas and the known volume of the vessel. The pressure recorded is that indicated by the manometer attached to the gas-collecting vessel. After evacuation of the right arm of the manometer, the mercury levels are adjusted by use of the leveling bulb to bring the meniscus in the left arm to a calibration point within the enlarged portion of the arm. The reason for this procedure is that the volume of the gas-collecting vessel, which includes the volume above the mercury in the left arm of the manometer, was determined with the mercury level at this indicated point.

The temperature of the bath surrounding the gas-collecting vessel is adjusted to 25°C prior to observing the pressure reading.

The gas-collecting system now is evacuated in readiness for collecting the gases of the reaction.

The stirring mechanism in the calorimeter is set into motion at a convenient time. When the level of the ammonia reaches to just below the ring-seal of the calorimeter the flow is shut off. The inlet tube is clamped shut and the ammonia supply connection is transferred to inlet tube 2 which is now unclamped. An amount of ammonia sufficient to cause gentle bubbling through the liquid is now admitted to the large Dewar through the tubing that leads to the bottom of the space between the two. The liquid ammonia at its boiling point is in equilibrium with its vapor and functions as a thermostat bath for the calorimeter.

During a period in which the temperature of the calorimeter

The total amount of ammonia collected in this way is calculated from the pressure of the gas and the known volume of the vessel. The pressure recorded is that indicated by the manometer attached to the gas-collecting vessel. After evacuation of the right arm of the manometer, the mercury levels are adjusted by use of the leveling bulb to bring the meniscus in the left arm to a calibration point within the enlarged portion of the arm. The reason for this procedure is that the volume of the gas-collecting vessel, which includes the volume above the mercury in the left arm of the manometer, was determined with the mercury level at this indicated point.

The temperature of the bath surrounding the gas-collecting vessel is adjusted to 50°C prior to observing the pressure reading.

The gas-collecting system now is evacuated in readiness for collecting the gases of the reaction.

The stirring mechanism in the calorimeter is set into motion at a convenient time. When the level of the ammonia reaches to just below the right-hand of the calorimeter the flow is shut off. The inlet tube is clamped shut and the ammonia supply connection is transferred to inlet tube B which is now unchanged. An amount of ammonia sufficient to cause gentle bubbling through the liquid is now admitted to the large neck through the tubing that leads to the bottom of the space between the two. The liquid ammonia at its boiling point is in equilibrium with its vapor and functions as a thermostat bath for the calorimeter.

During a period in which the temperature of the calorimeter

is approaching that of the thermostating bath, preparations of the thermocouple circuit are made. The reference junction is immersed in a small Dewar flask partly filled with distilled water and a quantity of crushed ice. The ice is prepared by crushing a piece of air-free ice and by washing the crushed pieces with distilled water. The mouth of the small Dewar flask is covered with a clean damp cloth to exclude entrance of contaminants.

The temperature measurements must be made regularly through a period preceding the initiation of the reaction, through the reaction period, and through a period that follows the end of the reaction. The temperature pattern thus obtained when temperature is plotted against time is utilized in evaluating the temperature change associated with the reaction.

In practice the temperatures are observed as scale readings of the galvanometer for respective potentiometer settings. They are observed at one minute intervals throughout the three periods as illustrated in the presentation of the data, Tables 3-10.

The battery circuit through the potentiometer is adjusted with reference to the standard cell.

When the rate of heat leak of the calorimeter and contents has attained a steady value as indicated by the constancy of the line pressure and the temperature of the calorimeter is slightly above that of the thermostating bath of ammonia for an endothermic reaction, observations of the temperature are commenced and continue throughout the three periods mentioned above.

Between observations of the scale readings of the galvano-

meter the pressure of the calorimeter line as indicated by the manometer is observed and tabulated. The barometric pressure is recorded along with the room temperature.

When a constant rate of temperature change has been observed for at least ten minutes the reaction is initiated by crushing the sample bulb beneath the surface of the liquid ammonia in the calorimeter. In this process, particular care is exercised in pushing on the sample-bulb rod to prevent breaking the rod, particularly if the fragile bulb offers resistance to the thrust of the rod. An intense blue color immediately becomes visible in the region of the sample bulb and vigorous bubbling through the solution of evolved hydrogen and of ammonia is seen. Except for occasional pressure surges of a few seconds' duration the line pressure is maintained constant to within 1-2 mm. by controlling the flow of the gases to the gas-collecting vessel through the needle valve. The scale readings of the galvanometer change very rapidly during the initial stages of the reaction. The scale readings are recorded throughout the period subsequent to cessation of the reaction until a constant rate of temperature change is again approached. The calorimeter line pressure is recorded at frequent intervals during this period following the reaction. Following the completion of the temperature measurements the pressure of the collected gases is determined at 25° C by means of a Gaertner cathetometer. Similarly the liquid level of the ammonia solution with respect to a fixed reference mark is determined.

After the pressure of the calorimeter has been recorded, the calorimeter is opened and the pressure is recorded along with the room temperature.

When a constant rate of temperature change has been observed for at least ten minutes the reaction is initiated by opening the sample bulb beneath the surface of the liquid ammonia in the calorimeter. In this process, particular care is exercised in pushing on the sample-bulb rod to prevent breaking the rod.

Particularly if the sample bulb offers resistance to the thrust of the rod, an intense blue color immediately becomes visible in the region of the sample bulb and vigorous bubbling through the solution of evolved hydrogen and of ammonia is seen. About

for occasional pressure changes of a few seconds' duration the line pressure is maintained constant to within 1-2 mm. by con-

trolling the flow of the gases to the gas-collecting vessel through the needle valve. The scale readings of the calorimeter change very rapidly during the initial stages of the reaction. The scale readings are recorded throughout the period

subsequent to cessation of the reaction until a constant rate of temperature change is again approached. The calorimeter line pressure is recorded at five minute intervals during this period

following the reaction. Following the completion of the calorimeter measurements the pressure of the collected gases is determined at 25° C by means of a Gasometer. Similarly the liquid level of the ammonia solution with respect to a fixed reference mark is determined.

Note with regard to special procedures involved in determining the heat of solution of lithium and the heat of solution of ammonium bromide.

The experimental procedure followed in determining the heat of solution of lithium metal and of ammonium bromide is substantially the same as that which has been fully described for determining the heats of reaction with the only point of difference being that no ammonium salt is initially dissolved in the liquid ammonia in the calorimeter. The sample bulbs contain, of course, metallic lithium and crystalline ammonium bromide respectively for the two determinations.

A small amount of lithium metal is used in the reaction. The weight of the metal is determined by weighing the sample bulb before and after the reaction. The weight of the ammonium bromide is determined by weighing the sample bulb before and after the reaction.

C. The weights of the small steel sample cylinder when full and when empty are recorded. The weight of ammonia is determined by the difference in these weights. A small amount of the ammonia transferred fills the calorimeter with vapor. The weight of this vapor is calculated from the known volume of the line and the pressure indicated by the manometer. (Determined for present line = 3.34 g)

D. Manometer readings of both the liquid ammonia meniscus and of a reference mark on the calorimeter wall are recorded. The reference mark is 176.7 mm. from the inside bottom of the calorimeter. The liquid height with respect to the bottom of the calorimeter is then calculated making use of the height of the reference mark.

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III. Presentation of the Data

The observations made in each experiment are recorded in the manner shown in the following tables. (tables 3-10)

A. Necessary data to determine the weight of alkali metal contained in each sample bulb include the weight and volume of the empty bulb and the weight of the filled bulb. The volume of the bulb is used in calculating the weight in vacuo of the sample:

$$\begin{array}{rcl} \text{wt} & = & \text{wt} + \text{vol of bulb} \times 0.00118 \\ \text{in vacuo} & & \text{obs} \end{array} \quad (4)$$

B. One mole of ammonium bromide is required for each gram-atom of alkali metal sample used in the reaction. The weight to the tenth of a milligram of ammonium bromide placed in the calorimeter is recorded.

C. The weights of the small steel ammonia cylinder when full and when empty are recorded. The weight of ammonia transferred to the calorimeter is then obtained as the difference in these weights. A small amount of the ammonia transferred fills the calorimeter line as vapor. The weight of this vapor is calculated from the known volume of the line and the pressure indicated by the manometer. (Determined for present line = 0.84 g)

D. Cathetometer readings of both the liquid ammonia meniscus and of a reference mark on the calorimeter wall are recorded. The reference mark is 176.7 mm. from the inside bottom of the calorimeter. The liquid height with respect to the bottom of the calorimeter is then calculated making use of the height of the reference mark.

E. Tabulation of the data obtained in making the temperature measurements includes the potentiometer settings and the galvanometer readings in scale divisions for each minute interval. Under the column headed notes is recorded besides the gas-collecting system data and the calorimeter line, manometer readings, any information that might have a possible bearing on the interpretation of the data.

1. Wt. of Mg used in filling calorimeter		2. Liquid height in calorimeter	
Wt. of Mg and cylinder	711.35 g	Galvanometer readings:	
Wt. of cylinder	327.85 g	Bottom of liquid meniscus	330.70 cm
Wt. of Mg	113.45 g	Reference mark	358.85 cm
Vol. of line	500 ml	Height of reference mark from bottom of calorimeter	178.7 cm
Wt. of Mg vapor in line	0.84 g	Height of liquid from bottom	148.2 cm
Wt. of Mg in calorimeter	112.69 g		

F. P.T.T. measurements

Potentiometer battery circuit balanced with respect to standard cell.

Galvanometer test point = 51.5 scale divisions

Time (minutes)	Potentiometer	Galvanometer	Notes
	AV	readings (Scale div.)	
			Ammonia vaporized from calorimeter during time of attaining temperature equilibrium.
			Gas-collecting system pressure:
			Barometer reading
			1-792.2 mm H-316.0 mm
			Bath temperature
			25.4 \pm 0.1 $^{\circ}\text{C}$
0	1131.3	51.5	Gas-collecting system evacuated
1		51.55	
2		51.55	

...whole lot of the best obtained in Spain and Portugal -
the manufacture included the most famous Spanish and Portuguese
...in Spain and Portugal for each article...
Under the name of the article is recorded...
the system used and the date of the...
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TABLE 3

EXPERIMENTAL DATA

EXPERIMENT C

DATE December 23, 1946
Determination of Heat of
Reaction of LITHIUM with
Ammonium Ion.

A. Wt. of Li sample

Wt. of bulb and Li	4.5570 g
Wt. of bulb	4.5170 g
Wt. of Li	0.0400 g
Vol. of bulb	2.23 ml
Wt. in vacuo (Li)	0.0426 g
Gram-atoms of Li	0.00615

B. Wt of NH_4Br used

No. gram-atoms	
Li x MW of NH_4Br	0.564 g
10% excess	0.056
Wt. required	0.620 g
Actual weight used	0.6271g

C. Wt of NH_3 used in filling calorimeter

Wt. of NH_3 and cylinder	711.35 g
Wt. of cylinder	597.89 g
Wt. of NH_3	113.46 g
Vol. of line	800 ml
Wt. of NH_3 vapor in line	0.84 g
Wt. of NH_3 in calorimeter	112.62 g

D. Liquid height in calorimeter

Cathetometer readings:

Bottom of liquid meniscus	330.70 mm
Reference mark	365.25 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	142.2 mm

E. E.M.F. measurements

Potentiometer battery circuit
balanced with respect to standard cell.

Galvanometer rest point = 51.6 scale divisions

Time (minutes)	Potentiometer μv	Galvanometer reading (Scale div.)	Notes
			Ammonia vaporized from calorimeter during time of attaining temperature equilibrium.
			Gas-collecting system pressure:
			Manometer reading
			L-795.9 mm R-516.0 mm
			Bath temperature
			$25 \pm 0.1^\circ\text{C}$
0	1121.0	51.6	Gas-collecting system
1		51.65	evacuated
2		51.55	

(minutes)	(uv)	(Scale div.)	Notes
3	1121.0	51.45	
4		51.4	
5		51.4	Calorimeter line pressure
6		51.4	Manometer reading
7		51.4	L-591.5 mm R-559.8 mm
8		51.45	
9		51.4	Erratic stirring
10		51.5	
11		51.35	
12		51.35	Constant stirring resumed
13		51.35	
14		51.35	
15		51.35	Calorimeter line pressure
16		51.35	Manometer reading
17		51.30	L-591.5 mm R-560.0 mm
18		51.6	
19		51.20	Stirrer stopped
20		51.15	
21		51.1	Stirrer resumed
22		50.85	
23		50.80	
24		50.65	
25		52.2	
26		50.65	
27	1122.0	52.2	Sample bulb crushed,
28	1125.5	19	reaction initiated
28 $\frac{1}{2}$	1154.0	54	
28 $\frac{1}{2}$	1154.0	55.2	
29	1154.0	54.5	Ammonia vaporized during
29 $\frac{1}{2}$		53.2	time of reaction
30		53.2	Gas-collecting system
30 $\frac{1}{2}$		52.2	pressure
31		51.85	Manometer reading
31 $\frac{1}{2}$		51.75	L-240.80 mm R-472.80 mm
32		51.75	Bath temperature $25 \pm 0.1^\circ\text{C}$
32 $\frac{1}{2}$	1154.0	52.0	
33		52.1	
33 $\frac{1}{2}$		52.2	
34		52.5	
34 $\frac{1}{2}$		52.65	Calorimeter line pressure
35		52.85	Manometer reading
35 $\frac{1}{2}$		53	L-592.5 mm R-559.0 mm
36		53.15	
36 $\frac{1}{2}$		53.45	
37		53.55	
37 $\frac{1}{2}$		53.80	

TABLE 4 EXPERIMENTAL DATA

EXPERIMENT E

DATE February 24, 1947

Determination of Heat of
Reaction of Lithium with
Ammonium Ion

A. Wt. of Li sample

Wt. of bulb and Li	3.3485 g
Wt. of bulb	<u>3.3335 g</u>
Wt. of Li	0.0150 g
Vol. of bulb	1.85 ml
Wt. of Li in vacuo	0.0172 g
Gram-atoms of Li	0.002478

B. Wt. of NH_4Br used

No. gram-atoms	
Li x MW of NH_4Br	0.2160 g
10% excess	<u>0.0216 g</u>
Wt. required	0.2376 g
Actual weight used	0.2429 g

C. Wt. of NH_3 used in
filling calorimeter

Wt. of NH_3 and cylinder	711.26 g
Wt. of cylinder	<u>597.53 g</u>
Wt. of NH_3	<u>113.73 g</u>
Vol. of line	900 ml
Wt. of NH_3 vapor in line	0.84 g

Wt. of NH_3 in calorimeter	112.89 g
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D. Liquid height in
calorimeter

Cathetometer readings:	
Bottom of liquid meniscus	741.4 mm
Reference mark	776.1 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid in bottom	142.0 mm

E. E.M.F. measurements

Potentiometer battery circuit
balanced with respect to standard cell.

Galvanometer rest point = 31.4 scale divisions

Time (minutes)	Potentiometer (uv)	Galvanometer reading (Scale div.)	Notes
			No ammonia vaporized from calorimeter during time of attaining temperature equilibrium
0	1120.0	30.3	Barometric pressure 760.0mm
1		30.1	
2		30.1	Calorimeter line pressure
3		30.1	Manometer reading
4	1125.0	38.5	L-598.5 mm R-553.5 mm
5		38.5	
6		38.6	Bath temperature $25 \pm 0.1^\circ\text{C}$

(minutes)	(uv)	(Scale div.)	Notes
7	1125.0	38.6	Barometer: 760.0 mm
8	1120.0	30.2	
9		30.1	Calorimeter line pressure
9 $\frac{1}{2}$		34.6	Manometer reading
9 $\frac{3}{4}$		21.0	L-598.5 mm R-553.5 mm
10 $\frac{1}{4}$	1130.0	32.6	
10 $\frac{1}{2}$	1130.0	30.3	At 9 minutes sample bulb
10 $\frac{3}{4}$	1140.0	45.8	crushed, reaction initiated.
11	1140.0	46.0	
11 $\frac{1}{4}$		45.6	
11 $\frac{1}{2}$		45.2	
11 $\frac{3}{4}$		44.8	
12		44.5	
12 $\frac{1}{2}$		44.2	
13		44.1	
13 $\frac{1}{2}$		44.2	
14		44.2	
15		44.3	
16		44.4	
17	1135.0	36.7	
18			
19		36.9	Blue solution noted around
20		37.1	broken sample bulb
21		37.3	
22		37.5	
23		37.7	Battery balanced; galvanome-
24		37.9	ter rest point 31.5
25			
26			
27	1135.0	38.4	
28		38.6	
29		38.7	
30		38.8	
31		39	
32	1130	39.2	
33		31.2	
34		31.4	
35		31.5	
36			
37		31.8	
38	1135.0	32.0	Ammonia vaporized during
39			time of reaction
			Gas-collecting system
			pressure
			Manometer reading
			L-653.2 mm R-744.4 mm
			Bath temperature 25 \pm 0.1°C

Station	(m)	(m)
Barometer: 750.0 mm	1135.0	7
Calibrated line pressure	1135.0	8
Barometer reading		9
1-500.0 mm 8-500.0 mm		10
40 2 minutes sample bulb	1135.0	11
exposed, recorded indicated	1135.0	12
		13
		14
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		16
		17
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TABLE 5 EXPERIMENTAL DATA

EXPERIMENT F

DATE March 21, 1947

Determination of Heat of
Reaction of LITHIUM with
Ammonium Ion

A. Wt. of Li sample

Wt. of bulb and Li	3.5145 g
Wt. of bulb	<u>3.4995</u> g
Wt. of Li	0.0150 g
Vol. of bulb	1.39 ml
Wt. of Li in vacuo	0.0166 g
Gram-atoms of Li	0.002395

B. Wt. of NH_4Br used

No. gram-atoms	
Li x MW of NH_4Br	0.212 g
10% excess	<u>0.021</u>
Wt. required	0.233 g
Actual weight used	0.2516g

C. Wt. of NH_3 used
in filling calorimeter

Wt. of NH_3 and cylinder	711.57 g
Wt. of cylinder	<u>597.52</u> g
Wt. of NH_3	114.05 g
Vol. of line	884 ml
Wt. of NH_3 vapor in line	0.84 g

Wt. of NH_3 in calori- meter	113.21 g
--	----------

D. Liquid height in
calorimeter

Cathetometer readings:	
Bottom of liquid meniscus	742.6 mm
Reference mark	778.4 mm

Height of reference mark from bottom of calorimeter	176.7 mm
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Height of liquid from bottom	140.9 mm
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E. E.M.F. measurements

Potentiometer battery circuit
balanced with respect to standard cell.

Galvanometer rest point = 35.0 scale divisions

Time (minutes)	Potential- meter (uv)	Galvanometer reading Scale div.	Notes
1	1135.0	36.0	Ammonia vaporized from
2			calorimeter during time of
3		35.7	attaining temperature
4		35.1	equilibrium.
5		34.6	Gas-collecting system
6	1140.0	42.7	pressure:
7		42.7	Manometer reading
8		42.7	L-794.0 mm R-794.0 mm
9		42.7	(No ammonia vaporized)

(minutes)	(μ v)	(Scale div.)	Notes
10		42.8	Calorimeter line pressure
11		42.9	Manometer reading
12		42.9	L- 586.0 mm R- 565.0 mm
13	1140.0		
14	1140.0	42.9	
15		43.0	Barometer: 757.5 mm
16		42.9	
17	1135.0	34.7	Battery balanced; galvanometer rest point 35.1
18	1135.0	34.7	
19		34.8	
20		34.8	Calorimeter line pressure
21		34.7	Manometer reading
22			L- 586.0 mm R- 565.0 mm
23		34.9	
24		35.0	Battery balanced; galvanometer rest point 35.0
25		34.8	
26	1145.0	34.9	
27		34.9	
28		34.9	Calorimeter line pressure
29		35.0	Manometer reading
30	1130.0	26.7	L- 775.4 mm R- 797.8 mm
31		26.7	
32		26.7	
33			Battery balanced; galvanometer rest point 34.9
34		26.9	
35		26.9	
36		26.9	
37	1130.0	26.8	
38			
39			Sample bulb crushed, reaction initiated.
40		18.0	
40 $\frac{1}{4}$	1135.0	21.0	
40 $\frac{1}{2}$	1140.0	25.6	
40 $\frac{3}{4}$	1145.0	33.0	
41	1145.0	29.6	
41 $\frac{1}{2}$	1150.0	34.5	
42	1150.0	32.0	
42 $\frac{1}{2}$	1150.0	32.0	
43	1150.0	32.0	
44		31.2	No more blue color.
44 $\frac{1}{2}$		30.9	Reaction over
45		31.0	
45 $\frac{1}{2}$		31.2	
46		31.4	
47		31.7	
48		31.9	Battery balanced; galvanometer rest point 34.9
49		32.3	
50			
51		32.9	
52		33.2	

Notes	(Scale div.)	(V)	(minutes)
Calorimeter line pressure	42.8		10
Manometer reading	42.9		11
1- 585.0 mm H- 585.0 mm	42.9		12
		1140.0	13
	42.9	1140.0	14
Barometer: 757.5 mm	42.9		15
	42.9		16
Battery balanced; galvanometer	42.7	1135.0	17
meter rest point 55.1	42.7		18
	42.8		19
Calorimeter line pressure	42.8		20
Manometer reading	42.7		21
1- 585.0 mm H- 585.0 mm			22
	42.8		23
Battery balanced; galvanometer	42.9		24
meter rest point 55.0	42.8		25
	42.8		26
	42.9		27
	42.9		28
	42.9		29
	42.7	1130.0	30
	42.7		31
	42.7		32
Battery balanced; galvanometer	42.9		33
meter rest point 54.9	42.9		34
	42.9		35
	42.9		36
	42.8	1130.0	37
			38
Sample bulb crushed, reaction			39
initiated.	18.0		40
	21.0	1135.0	41
	25.8	1140.0	42
	25.0	1145.0	43
	29.8	1145.0	44
	34.8	1150.0	45
	32.0	1150.0	46
	32.0	1150.0	47
	32.0	1150.0	48
No more blue color.	31.8		49
Reaction over	30.9		50
	31.0		51
	31.3		52
	31.4		53
	31.7		54
Battery balanced; galvanometer	31.9		55
meter rest point 54.9	32.0		56
	32.8		57
	32.8		58

(minutes) (μv) (Scale div.)

Notes

53 33.5

54 33.8

55 34.1

56 34.3

57 1145.0 26.5

58 26.7

59 26.9

60 27.2

61 1150.0 35.7

62 35.9

63 36.2

64 36.4

65 37.0

66 37.1

67 37.3

68 29.3

69 1145.0 29.5

70 29.7

71 29.8

72 30.1

73

Battery balanced; galvanometer rest point 35.0

Calorimeter line pressure
Manometer reading
L- 776.4 mm R- 797.8 mm

Ammonia vaporized during
time of reaction

Gas-collecting system
pressure

Manometer reading

L-663.6 mm R-765.5 mm

Bath temperature $25 \pm 0.1^\circ \text{C}$

Time Potential- Galvanometer
(minutes) meter (μv) reading
(Scale div.)

Notes

0 1150.0 36.3

1 36.1

2 36.1

3 36.9

4 36.9

5 1145.0 37.7

No ammonia vaporized from
calorimeter during time of
attaining temperature
equilibrium.

Calorimeter line pressure
Manometer reading
L- 596.5 mm R- 655.0 mm

Notes	(Scale div.)	(ev)	(minutes)
	33.5		55
	33.8		54
	34.1		53
	34.3		52
	34.5	1143.0	51
	34.7		50
	34.9		49
	35.1		48
	35.3	1150.0	47
	35.5		46
	35.7		45
	35.9		44
	36.1		43
Battery balanced; galvanometer rest point 35.0	37.0		42
	37.1		41
	37.2		40
	37.3	1152.0	39
	37.4		38
	37.5		37
	37.6		36
	37.7		35
Calorimeter line pressure	37.8		34
Manometer reading	37.9		33
I-775.4 mm R-797.8 mm	38.0		32

Ammonia vaporized during
 time of test
 Gas-liquid system
 pressure
 amount of gas
 I-775.4 mm R-797.8 mm
 each temperature 35.0, 37.0

TABLE 6 EXPERIMENTAL DATA

EXPERIMENT G

DATE March 24, 1947
Determination of Heat
of Reaction of LITHIUM
WITH AMMONIUM ION.

A. Wt. of Li sample

Wt. of bulb and Li	3.3046 g
Wt. of bulb	<u>3.2742 g</u>
Wt. of Li	0.0304 g
Vol. of bulb	1.43 ml
Wt. of Li in vacuo	0.0321 g
Gram-atoms of Li	0.00463

B. Wt. of NH_4Br used

No. gram-atoms	
Li x MW of NH_4Br	0.430 g
10% excess	<u>0.043</u>
Wt. required	0.473 g
Actual weight used	0.5168g

C. Wt. of NH_3 used in filling calorimeter

Wt. of NH_3 and cylinder	711.32 g
Wt. of cylinder	<u>597.51 g</u>
Wt. of NH_3	113.81 g
Vol. of line	800 ml
Wt. of NH_3 vapor in line	0.84 g
Wt. of NH_3 in calorimeter	112.97 g

D. Liquid height in calorimeter

Cathetometer readings:	
Bottom of liquid meniscus	753.0 mm
Reference mark	788.15mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	141.5 mm

E. E.M.F. measurements

Potentiometer battery circuit
balanced with respect to
standard cell.

Galvanometer rest point
Scale division = 32.7

Time (minutes)	Potential- meter (μv)	Galvanometer reading (Scale div.)
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Notes

No ammonia vaporized from
calorimeter during time of
attaining temperature
equilibrium.

0	1120.0	36.3
1		36.1
2		36.1
3		35.9
4		35.9
5	1115.0	27.7

Calorimeter line pressure
Manometer reading
L- 598.5 mm R- 553.8 mm

TABLE 6
EXPERIMENTAL DATA

EXPERIMENT 6 DATA March 28, 1947 Determination of Heat of Reaction of LITHIUM WITH AMMONIA ION.			
A. Wt. of Li sample		B. Wt. of NH ₃ used	
Wt. of bulb and Li	5.5546 g	No. gram-atom	
Wt. of bulb	3.3742 g	Li x Wt of NH ₃	0.433 g
Wt. of Li	2.1804 g		
Vol. of bulb	1.43 ml	10% excess	0.043
Wt. of Li in vacuum	0.0321 g	Wt. required	0.473 g
Gram-atom of Li	0.00463	Actual weight used	0.5153 g
C. Wt. of NH ₃ used in filling calorimeter		D. Liquid height in calorimeter	
Wt. of NH ₃ and cylinder	711.32 g	Calorimeter reading:	
Wt. of cylinder	597.51 g	Bottom of liquid meniscus	753.0 mm
Wt. of NH ₃	113.81 g	Reference mark	788.15 mm
Vol. of line	800 ml		
Wt. of NH ₃ vapor in line	0.84 g	Height of reference mark from bottom of calorimeter	176.7 mm
Wt. of NH ₃ in calorimeter	112.97 g	Height of liquid from bottom	141.5 mm
E. E.M.F. measurements			
Potentiometer battery circuit balanced with respect to standard cell.			
Galvanometer rest point Scale division = 32.7			
Time (minutes)	Potential meter (mv)	Galvanometer reading	Notes
0	1180.0	36.3	No ammonia vaporized from calorimeter during time of attaining temperature equilibrium.
1		36.1	
2		36.1	
3		35.9	
4		35.9	
5	1115.0	37.7	Calorimeter line accurate Galvanometer reading 1- 358.5 mm H ₂ - 553.0 mm

(minutes)	(μ v)	(Scale div.)	Notes
6		27.7	Barometer: 745.6 mm
7		27.5	
8		27.7	
9		27.1	Battery balanced; galvanometer rest point 32.7
10			
11		27.1	
12	1120.0	34.7	
13		34.6	
14		34.6	
15		34.5	
16		34.3	
17		34.3	
18		34.2	
19			Galvanometer swinging
20			
21	1150.0		
22			
23			
24			
25			Battery balanced; galvanometer rest point 32.6
26	1120.0	33.1	
27		33.4	
28	1120.0	32.8	
29		32.7	Calorimeter line pressure
30		32.5	Manometer reading
31		32.5	L- 596.9 mm R- 555.0 mm
32		32.4	
33	1125.0	40.8	Battery balanced; galvanometer rest point 32.6
34		40.6	
35		40.5	
36		40.5	
37		40.4	Sample bulb crushed, reaction initiated
37 $\frac{1}{4}$		39.6	
37 $\frac{1}{2}$		39.9	
38		38.0	
38 $\frac{1}{4}$		27.0	
38 $\frac{1}{2}$		12.0	
38 $\frac{3}{4}$	1135.0	20.0	
39	1145.0	31.5	
39 $\frac{1}{4}$		30.1	
39 $\frac{1}{2}$		27.1	
39 $\frac{3}{4}$		24.5	
40	1155.0	39.4	
40 $\frac{1}{2}$		39.0	
41		39.5	
41 $\frac{1}{2}$		37.8	
42		37.4	
42 $\frac{1}{2}$		37.0	Reaction over
43		37.2	Battery balanced; galvanometer rest point 32.9
44		37.3	

(minutes)	(mv)	(scale div.)	Notes
6			Barometer: 745.6
7			
8			
9			Battery balanced; galvanometer rest point 32.7
10			
11			
12	1120.0		
13			
14			
15			
16			
17			
18			Galvanometer swinging
19			
20			
21			
22			
23			
24			Battery balanced; galvanometer rest point 32.6
25	1120.0		
26			
27			
28	1120.0		Colorimeter line pressure
29			Manometer reading
30			I-525.9 mm H-525.0 mm
31			
32			
33	1120.0		Battery balanced; galvanometer rest point 32.6
34			
35			
36			
37			Sample bulb crushed
38			Reaction initiated
39			
40			
41			
42			
43			
44			
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47			
48			
49			
50	1120.0		
51			
52			
53			
54			
55			
56			
57			
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(minutes)	(μ v)	(Scale div.)	Notes
45		37.5	Blue color in neck of
46		37.7	sample bulb
47		38.0	
48		38.2	Calorimeter line pressure
49		38.6	Manometer reading
50			L- 597.5 mm R- 554.5 mm
51			
52			Battery balanced; galvano-
53			meter rest point 33.1
54		40.1	
55		40.4	
56		40.6	Battery balanced; galvano-
57		40.5	meter rest point 33.2
58		40.7	
59	1150.0	32.9	
60		33.2	Battery balanced; galvano-
			meter rest point 33.1
			Ammonia vaporized from
			calorimeter during reaction
			period
			Gas-collecting system
			pressure:
			Manometer reading
			L- 661.7 mm R- 851.7 mm
			Bath temperature
			25 \pm 0.1° C

Time	Ammonia	Calorimeter	Notes
(minutes)	(μ v)	reading	
		(See a div.)	
1			Ammonia vaporized from
2			calorimeter during time of
3	1150.0	33.0	attaining temperature
4		33.4	equilibrium
5		33.5	Gas-collecting system
6			pressure:
7		33.6	Manometer reading
8			L- 751.8 mm R- 876.7 mm
			Bath temperature 25 \pm 0.1° C

(minutes)	(wt)	(Scale div.)	Notes
42		37.5	Blue color in neck of
43		37.7	sample bulb
44		38.0	
45		38.2	Calorimeter line pressure
46		38.4	Manometer reading
47		38.6	1- 297.5 mm H- 334.5 mm
48			
49			Battery balanced; galvanometer rest point 33.1
50			
51			
52			
53		40.1	
54		40.4	
55		40.6	Battery balanced; galvanometer rest point 33.2
56		40.8	
57		40.7	
58		39.9	
59	1150.0	39.2	Battery balanced; galvanometer rest point 33.1
60			
			Ammonia vaporized from
			calorimeter during reaction
			period
			Gas-collecting system
			pressure:
			Manometer reading
			1- 331.7 mm H- 331.7 mm
			Bath temperature
			25.40 ± 0.1 °C

TABLE 7

EXPERIMENTAL DATA

EXPERIMENT A

DATE July 18, 1947

Determination of Heat
of Reaction of CESIUM
with Ammonium Ion

A. Wt. of Cs. sample

Wt. of bulb and Cs	3.9390 g
Wt. of bulb	<u>3.1645 g</u>
Wt. of Cs	<u>0.1645</u>
Vol. of bulb	1.75 g
Wt. of Cs in vacuo	0.7766
Gram-atoms of Cs	0.005848

B. Wt. of NH_4Br used

No. gram-atoms	
Cs x MW of NH_4Br	0.570 g
10% excess	<u>0.057 g</u>
Wt. required	<u>0.627 g</u>
Actual weight used	0.628 g

C. Wt. of NH_3 used in
filling calorimeter

Wt. of NH_3 and cylinder	711.30 g
Wt. of cylinder	<u>597.45 g</u>
Wt. of NH_3	<u>113.85 g</u>
Vol. of line	800 ml
Wt. of NH_3 vapor in line	0.84 g
Wt. of NH_3 in calorimeter	113.01 g

D. Liquid Height in
Calorimeter

Cathetometer readings:	
Bottom of liquid meniscus	752.9 mm.
Reference mark	789.7 mm.
Height of reference mark from bottom of calorimeter	176.7 mm.
Height of liquid from bottom	139.9 mm.

E. E.M.F. measurements

Potentiometer battery circuit
balanced with respect to standard cell.

Galvanometer rest point = 43.9 scale divisions

Time (minutes)	Potential- meter (uv)	Galvanometer reading (Scale div.)	Notes
0			Ammonia vaporized from
1			calorimeter during time of
2	1130.0	45.5	attaining temperature
3		45.4	equilibrium
4		45.5	Gas-collecting system
5			pressure:
6		45.5	Manometer reading
7			L- 794.8 mm. R- 576.7 mm
8			

Bath temperature $25 \pm 0.1^\circ\text{C}$

EXPERIMENT A
DATE July 18, 1947
Determination of heat
of reaction of CESTUM
with ammonium ion
5. wt. of 10% aq. ammonia

EXPERIMENTAL DATA

TABLE 7

A. wt. of C. sample		B. wt. of 10% aq. ammonia	
wt. of bulb and its 2.0380 g		wt. of ammonia 0.570 g	
wt. of bulb 2.1625 g			
wt. of C. 0.1643 g			
Vol. of bulb 1.75 cc			
wt. of C. in vapor 0.7368 g			
Gravimetric of C. 0.005848 g			
C. wt. of 10% used in filling calorimeter		D. Liquid level in Calorimeter	
wt. of 10% and cylinder 711.50 g		Calorimeter	
wt. of cylinder 697.48 g		Reading: Bottom of liquid 752.9 mm.	
wt. of 10% 113.85 g		Reference mark 752.4 mm.	
Vol. of line 800 ml		Height of reference mark from bottom of calorimeter 176.7 mm.	
wt. of 10% vapor in line 0.84 g		Height of liquid from bottom 130.9 mm.	
wt. of 10% to calorimeter 113.01 g			
E. A. S. measurements			
Potentiometer battery circuit balanced with respect to standard cell.			
Silver-silver chloride test point = 45.9 scale divisions			
Time	Potential - (mV)	Calorimeter - (mV)	Notes
0			Ammonia vaporized from calorimeter during time of reading
1			
2	1130.0	45.9	Reading temperature equalized
3		45.4	
4		45.9	Gas collecting system pressure
5			
6		45.9	Calorimeter reading
7			11-724.8 mm. H- 525.7 mm.
8			
Room temperature 25.0-26.0°C			

(minutes)	(uv)	(Scale div.)	Notes
9	1130.0	45.5	Stirring about 72/min.
10		45.5	
11		45.5	Gas-coll. system evacuated
12	1125.0	38.9	Battery balanced; galvanometer rest point 43.9
13		38.9	
14		38.9	
15		38.9	Calorimeter line pressure
16		38.9	Manometer reading
17		39.0	L-588.0 mm R-562.3 mm
18		39.0	
19		39.0	Barometer: 756.1 mm
20		39.1	
21	1130.0	39.1	Battery balanced; galvanometer rest point 43.8
22		45.8	
23			
24	1130.0	46.0	Calorimeter line pressure
25		46.0	Manometer reading
26		46.0	L-589.0 mm R-562.0 mm
27		46.1	
28		46.0	
29		46.1	
30		46.0	
31		46.1	Sample bulb crushed
32		46.1	Reaction initiated
33		45.8	
34			
35	1130.0	42.0	
36	1140.0	46.9	
37		39.1	Battery balanced; galvanometer rest point 43.8
38	1150.0	47.9	
39		45.3	
40		42.0	
41		37.5	Bubbling stopped
42		45.6	
43 $\frac{1}{2}$		44.6	More reaction
44 $\frac{1}{2}$		45.0	
45	1160.0	46.6	
46		44.2	
47		42.4	
48 $\frac{1}{2}$	1165.0	42.5	
49		41.5	
50		48.0	
51		48.1	
52		48.4	
53		49.1	
54	1165.0	48.2	
55		45.5	
56		48.8	
57		49.8	

		(Scale Div.)	(V)	(Amperes)
Relative Mount Voltage	43.5	1150.0		10
	43.5			11
	43.5			12
	43.5			13
	43.5			14
	43.5			15
	43.5			16
	43.5			17
	43.5			18
	43.5			19
Batteries balanced; battery meter test point 43.5	43.5	1150.0		20
	43.5			21
	43.5			22
	43.5			23
	43.5			24
	43.5			25
	43.5			26
	43.5			27
	43.5			28
	43.5			29
Calorimeter life pressure	43.5	1150.0		30
	43.5			31
	43.5			32
	43.5			33
	43.5			34
	43.5			35
	43.5			36
	43.5			37
	43.5			38
	43.5			39
Batteries balanced; battery meter test point 43.5	43.5	1150.0		40
	43.5			41
	43.5			42
	43.5			43
	43.5			44
	43.5			45
	43.5			46
	43.5			47
	43.5			48
	43.5			49
Calorimeter life pressure	43.5	1150.0		50
	43.5			51
	43.5			52
	43.5			53
	43.5			54
	43.5			55
	43.5			56
	43.5			57
	43.5			58
	43.5			59
Batteries balanced; battery meter test point 43.5	43.5	1150.0		60
	43.5			61
	43.5			62
	43.5			63
	43.5			64
	43.5			65
	43.5			66
	43.5			67
	43.5			68
	43.5			69
Calorimeter life pressure	43.5	1150.0		70
	43.5			71
	43.5			72
	43.5			73
	43.5			74
	43.5			75
	43.5			76
	43.5			77
	43.5			78
	43.5			79
Batteries balanced; battery meter test point 43.5	43.5	1150.0		80
	43.5			81
	43.5			82
	43.5			83
	43.5			84
	43.5			85
	43.5			86
	43.5			87
	43.5			88
	43.5			89
Calorimeter life pressure	43.5	1150.0		90
	43.5			91
	43.5			92
	43.5			93
	43.5			94
	43.5			95
	43.5			96
	43.5			97
	43.5			98
	43.5			99

(minutes)	(μ v)	(Scale div.)	Notes
58		50.6	
59		50.6	
60		51.1	
61		51.6	
62	1155.0	39.0	
63		43.9	
64		39.6	Calorimeter line pressure
65		39.9	Manometer reading
66	1155.0	40.2	L- 592.6 mm R- 558.3 mm
67		40.6	
68		41.0	
69		41.2	
70		41.5	
71		41.8	
72		42.1	
73	1160.0	49.0	Battery balanced; galvanometer rest point 43.8
74		49.3	
75		49.6	
76	1155.0	43.2	
77		43.5	
78		43.8	
79		44.0	
80			Ammonia vaporized from calorimeter during heat of reaction
			Gas-collecting system pressure:
			Manometer reading
			L- 669.8 mm R- 875.0 mm
			Bath temperature
			$25 \pm 0.1^\circ\text{C}$

Time (minutes)	Potentiometer (μ v)	Galvanometer reading (Scale div.)	Notes
31	1120.0	53.5	Ammonia vaporized from calorimeter during time of attaining temperature equilibrium
32		53.6	
33		53.6	
34		53.7	
35		53.7	Gas-collecting system pressure:
36		53.7	Manometer reading
37		53.7	L- 788.1 mm R- 563.9 mm
38		53.8	Bath temperature $25 \pm 0.1^\circ\text{C}$
39		53.8	

Notes	(Scale Div.)	(mv)	(microns)
Calorimeter line pressure manometer reading I-522.5 mm R-522.5 mm	50.5	1155.0	58
	50.5		59
	51.1		60
	51.5		61
	52.0		62
	52.5		63
	53.0		64
	53.5		65
	54.0		66
	54.5		67
Battery balanced; calvano- meter rest point 45.8	55.0	1155.0	68
	55.5		69
	56.0		70
	56.5		71
	57.0		72
	57.5		73
	58.0		74
	58.5		75
	59.0		76
	59.5		77
Ammonia vaporized from calorimeter during heat of reaction Gas-collecting system pressure: manometer reading I-509.5 mm R-509.5 mm Bath temperature 23.0°C	60.0	1155.0	78
	60.5		79
	61.0		80
	61.5		81
	62.0		82
	62.5		83
	63.0		84
	63.5		85
	64.0		86
	64.5		87

TABLE 8 EXPERIMENTAL DATA

EXPERIMENT C (CESIUM)

DATE July 24, 1947

Determination of Heat of
Reaction of CESIUM WITH
AMMONIUM ION

A. Wt. of Cs sample

Wt. of bulb and Cs	4.5158 g
Wt. of bulb	<u>3.4956 g</u>
Wt. of Cs	<u>1.0202 g</u>
Vol. of bulb	1.66 ml
Wt. of Cs in vacuo	1.1843 g
Gram-atoms of Cs	0.008917

B. Wt. of NH_4Br used

No. gram-atoms	
Cs x MW of NH_4Br	0.873 g
10% excess	<u>0.087 g</u>
Wt. required	<u>0.960 g</u>
Actual weight used	0.966 g

C. Wt. of NH_3 used in
filling calorimeter

Wt. of NH_3 and cylinder	711.38 g
Wt. of cylinder	<u>597.40 g</u>
Wt. of NH_3	<u>113.98 g</u>
Vol. of line	800 ml
Wt. of NH_3 vapor in line	0.84 g
Wt. of NH_3 in calorimeter	113.14 g

D. Liquid height in
calorimeter

Cathetometer readings:	
Bottom of liquid meniscus	752.6 mm
Reference mark	789.6 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	139.7 mm

E. E.M.F. measurements

Potentiometer battery circuit
balanced with respect to
standard cell.

Galvanometer rest point
Scale division = 52.1

Time (minutes)	Potentiometer (μv)	Galvanometer reading (Scale div.)	Notes
21	1120.0	59.5	Ammonia vaporized from calorimeter during time of attaining temperature equilibrium
22		59.6	
23		59.6	
24		59.7	Gas-collecting system pressure:
25		59.7	
26		59.7	Manometer reading
27		59.7	
28		59.8	L- 796.1 mm R- 563.9 mm
29		59.8	Bath temperature $25 \pm 0.1^\circ\text{C}$

EXPERIMENTAL DATA
 DATE: July 24, 1947
 Location: Station of Heat of
 Reaction of Oxidation with
 Ammonia Ion

A. Wt. of Co sample		B. Wt. of NH ₃ used	
Wt. of bulb and Co	4.515 g	No. of samples	0.87 g
Wt. of bulb	3.435 g	Co x Wt. of NH ₃	0.87 g
Wt. of Co	1.080 g		
Vol. of bulb	1.55 ml	10% excess	0.097 g
Wt. of Co in vacuo	1.183 g	Wt. required	0.960 g
Gram-atoms of Co	0.00891	Actual weight used	0.965 g
C. Wt. of NH ₃ used in filling calorimeter		D. Liquid height in calorimeter	
Wt. of NH ₃ and cylinder	711.38 g	Calorimeter	
Wt. of cylinder	537.40 g	Reading	
Wt. of NH ₃	173.98 g	Bottom of liquid	752.8 mm
Vol. of liquid	800 ml	Reference mark	789.8 mm
Wt. of NH ₃ vapor in line	0.84 g	Height of reference mark from bottom of calorimeter	175.7 mm
Wt. of NH ₃ in calorimeter	173.14 g	Height of liquid from bottom	139.7 mm
E. N.H.P. measurements			
Potentiometer battery circuit balanced with respect to standard cell.			
Calorimeter test point scale division = 52.1			
Time (minutes)	Potentiometer Reading (mv)	Calorimeter Reading (Scale div.)	Notes
21	1720.0	52.5	Ammonia vaporized from calorimeter during time of
22		52.6	attaining temperature equilibrium
23		52.7	Gas-collecting system
24		52.7	Pressure
25		52.7	Manometer reading
26		52.7	I-V 25.1 mm H ₂ O = 52.5 mm
27		52.8	Water temperature 23 ± 0.1°
28		52.8	

(minutes)	(μ v)	(Scale div.)	Notes
30		59.8	Gas-coll. system evacuated
31	1120.0	59.8	Battery balanced; galvanometer rest point 52.2
32		59.8	
33	1115.0	52.5	
34		52.5	
35		52.5	
36		52.6	
37	1120.0	59.9	Calorimeter line pressure
38			Manometer reading
39			L- 587.6 mm R- 563.9 mm
40		60.0	
41		59.9	Battery balanced; galvanometer rest point 52.1
42			
43		60.0	
44		60.0	
45		60.0	
46	1115.0	52.7	
47		52.7	
48		52.7	
49		52.7	
50			Calorimeter line pressure
51			Manometer reading
52			L- 587.6 mm R- 563.9 mm
53			
54		52.7	
55		52.7	Sample bulb crushed
55 $\frac{1}{2}$		53	Reaction initiated
55 $\frac{1}{2}$		55.7	
55 $\frac{3}{4}$		55.4	Needle valve open
56		57.5	
56 $\frac{1}{4}$		60.0	
56 $\frac{1}{2}$		55.0	
56 $\frac{3}{4}$		45.0	
57		42.2	
57 $\frac{1}{4}$		39.2	
57 $\frac{1}{2}$		36.7	
57 $\frac{3}{4}$		34.2	
58		31.8	
58 $\frac{1}{2}$	1135.0	57.4	
58 $\frac{3}{4}$		55.7	
59		54.2	
59 $\frac{1}{4}$		51.2	
59 $\frac{1}{2}$		49.2	
59 $\frac{3}{4}$		47.8	
60 $\frac{1}{4}$		44.0	
60 $\frac{1}{2}$		55.8	
60 $\frac{3}{4}$		53.8	
61	1144.0	55.3	
62		52.3	
63		51.4	

Item	Quantity	Unit Price	Total Price
1. 1000	1000	1.00	1000.00
2. 500	500	0.50	250.00
3. 250	250	0.25	62.50
4. 125	125	0.125	15.625
5. 62.5	62.5	0.0625	3.90625
6. 31.25	31.25	0.03125	0.9765625
7. 15.625	15.625	0.015625	0.244140625
8. 7.8125	7.8125	0.0078125	0.06103515625
9. 3.90625	3.90625	0.00390625	0.015234375
10. 1.953125	1.953125	0.001953125	0.003828125
11. 0.9765625	0.9765625	0.0009765625	0.00095703125
12. 0.48828125	0.48828125	0.00048828125	0.00023828125
13. 0.244140625	0.244140625	0.000244140625	0.000059609375
14. 0.1220703125	0.1220703125	0.0001220703125	0.00001490234375
15. 0.06103515625	0.06103515625	0.00006103515625	0.00000372607421875
16. 0.030517578125	0.030517578125	0.000030517578125	0.00000093017578125
17. 0.0152587890625	0.0152587890625	0.0000152587890625	0.00000023193359375
18. 0.00762939453125	0.00762939453125	0.00000762939453125	0.0000000579345703125
19. 0.003814697265625	0.003814697265625	0.000003814697265625	0.00000001438328125
20. 0.0019073486328125	0.0019073486328125	0.0000019073486328125	0.0000000035958984375
21. 0.00095367431640625	0.00095367431640625	0.00000095367431640625	0.0000000008984375
22. 0.000476837158203125	0.000476837158203125	0.000000476837158203125	0.000000000224119140625
23. 0.0002384185791015625	0.0002384185791015625	0.0000002384185791015625	0.0000000001120595703125
24. 0.00011920928955078125	0.00011920928955078125	0.00000011920928955078125	0.00000000005602978515625
25. 0.000059604644775390625	0.000059604644775390625	0.000000059604644775390625	0.000000000028014892578125
26. 0.0000298023223876953125	0.0000298023223876953125	0.0000000298023223876953125	0.0000000000140074462890625
27. 0.00001490116119384765625	0.00001490116119384765625	0.00000001490116119384765625	0.00000000000700372314453125
28. 0.000007450580596923828125	0.000007450580596923828125	0.000000007450580596923828125	0.000000000003501861572265625
29. 0.0000037252902984619140625	0.0000037252902984619140625	0.0000000037252902984619140625	0.0000000000017509307861328125
30. 0.00000186264514923095703125	0.00000186264514923095703125	0.00000000186264514923095703125	0.00000000000087546539306640625
31. 0.000000931322574615478515625	0.000000931322574615478515625	0.000000000931322574615478515625	0.000000000000437732696533203125
32. 0.0000004656612873077392578125	0.0000004656612873077392578125	0.0000000004656612873077392578125	0.0000000000002188663482666015625
33. 0.00000023283064365386962890625	0.00000023283064365386962890625	0.00000000023283064365386962890625	0.00000000000010943317413330078125
34. 0.000000116415321826934814453125	0.000000116415321826934814453125	0.000000000116415321826934814453125	0.000000000000054716587066650390625
35. 0.0000000582076609134674072265625	0.0000000582076609134674072265625	0.000000000582076609134674072265625	0.0000000000000273582935333251953125
36. 0.00000002910383045673370361328125	0.00000002910383045673370361328125	0.0000000002910383045673370361328125	0.00000000000001367914676666259765625
37. 0.000000014551915228366851806640625	0.000000014551915228366851806640625	0.00000000014551915228366851806640625	0.0000000000

(minutes)	(μ v)	(Scale div.)	Notes
63 $\frac{1}{4}$		50.8	
63 $\frac{3}{8}$		61.0	
63 $\frac{1}{2}$		68.0	
64 $\frac{1}{4}$		51.5	Rapid temperature change
65	1138.0	50.3	
65 $\frac{1}{2}$		52.4	
66	1140.0	49.5	
66 $\frac{1}{4}$		48.8	
66 $\frac{1}{2}$		48.1	
67		47.0	Reaction over
67 $\frac{1}{2}$	1144.0	52.8	
67 $\frac{3}{4}$		53.1	
68		53.7	
68 $\frac{1}{8}$		53.8	
68 $\frac{1}{4}$		53.2	
69		52.8	
69 $\frac{1}{2}$		52.9	
70 $\frac{1}{4}$		53.3	
71	1145.0	52.1	Still going
71 $\frac{1}{2}$		50.1	
72		49.8	
72 $\frac{1}{2}$		58.0	
73		54.2	
74 $\frac{1}{2}$		50.2	
75		50.7	
76 $\frac{1}{2}$		49.8	
77 $\frac{1}{2}$		49.7	Barometer: 770.0 mm
78	1147.0	52.8	
79 $\frac{1}{2}$		53.4	
80		53.7	
81		54.0	Apparently over
82		53.4	
83		53.7	
84		54.2	
85		54.5	Battery needed balancing
86		55.5	
87		55.7	Battery balanced; galvan-
88		56.0	ometer rest point 51.9
89		56.4	
90		56.8	Calorimeter line pressure
91		57.2	Manometer reading
92		50.3	L-588.2 mm R-563.4 mm
93	1142.0	50.7	Ammonia vaporized from calorimeter during reaction Gas-collecting system pressure Manometer reading L-670.9 mm R-946.6 mm Bath temperature 25 \pm 0.1

(minutes)	(mv)	(Scale div.)	Notes
63		50.8	
63		51.0	
63		58.0	
64		51.5	Read temperature change
65	1138.0	50.3	
65		52.4	
65		49.8	
66	1140.0	48.8	
66		48.1	
67		47.0	Reaction over
67	1144.0	52.8	
67		53.1	
68		53.7	
68		52.8	
68		52.2	
69		52.8	
69		52.9	
70		53.3	
70	1145.0	52.1	Still going
71		50.1	
71		49.8	
72		58.0	
72		54.2	
73		50.2	
73		50.7	
74		49.8	
74		49.7	Barometer: 770.0 mm
75	1147.0	52.5	
75		53.4	
76		53.7	
76		54.0	Apparently over
77		53.4	
77		53.7	
78		54.2	
78		54.5	Battery needed balancing
79		55.2	
79		55.7	Battery balanced; galvan-
80		56.0	ometer rest point 51.9
80		56.4	
81		56.6	Calorimeter line pressure
81		57.2	Manometer reading
82		50.2	I-588.2 mm H-563.4 mm
82	1148.0	50.7	
83			Ammonia vaporized from
83			calorimeter during
83			reaction
83			Gas-collecting system
83			pressure
83			Manometer reading
83			I-570.8 mm H-546.8 mm
83			Bath temperature 25.0.1

TABLE 9 EXPERIMENTAL DATA

DATE August 9, 1947
 Determination of Heat of
 Solution of LITHIUM with
 Liquid Ammonia

A. Wt. of Li sample

Wt. of bulb and Li	8.0447 g
Wt. of bulb	<u>7.5530 g</u>
Wt. of Li	0.4917 g
Vol. of bulb	5.1 ml
Wt. of Li in vacuo	0.4977 g
Gram-atoms of Li	0.0718 g

B. No Ammonium Bromide used

C. Wt. of NH_3 used in filling calorimeter

Wt. of NH_3 and cylinder	711.05 g
Wt. of cylinder	<u>597.41 g</u>
Wt. of NH_3	113.64 g
Vol. of line	800 ml
Wt. of NH_3 vapor in line	0.84 g
Wt. of NH_3 in calorimeter	112.80 g

D. Liquid height in calorimeter

Cathetometer readings:	
Bottom of liquid meniscus	749.3 mm
Reference mark	781.1 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	144.9 mm

E. E.M.F. measurements

Potentiometer battery circuit
 balanced with respect to standard cell.

Galvanometer rest point = 46.6 scale divisions

Time (minutes)	Potential- meter (uv)	Galvanometer reading (Scale div.)	Notes
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Ammonia vaporized from
 calorimeter during time of
 attaining temperature
 equilibrium.

Gas-collecting system
 pressure
 Manometer reading
 L-661.9 mm R-836.2 mm

Bath temperature $25 \pm 0.1^\circ \text{C}$

DATE August 9, 1947
Determination of heat of
solution of LITHIUM with
liquid ammonia

TABLE V - CALORIMETRIC DATA

A. Heat of solution of lithium in liquid ammonia		B. Heat of solution of lithium in liquid ammonia	
Weight of lithium, g.	0.0472	Weight of lithium, g.	0.0472
Weight of ammonia, g.	7.5250	Weight of ammonia, g.	7.5250
Weight of solution, g.	7.5722	Weight of solution, g.	7.5722
Volume of solution, ml.	8.1	Volume of solution, ml.	8.1
Temperature of solution, °C.	0.4377	Temperature of solution, °C.	0.4377
Heat of solution, cal/g.	0.0718	Heat of solution, cal/g.	0.0718
C. Heat of solution of lithium in liquid ammonia		D. Heat of solution of lithium in liquid ammonia	
Weight of lithium, g.	0.0472	Weight of lithium, g.	0.0472
Weight of ammonia, g.	7.5250	Weight of ammonia, g.	7.5250
Weight of solution, g.	7.5722	Weight of solution, g.	7.5722
Volume of solution, ml.	8.1	Volume of solution, ml.	8.1
Temperature of solution, °C.	0.4377	Temperature of solution, °C.	0.4377
Heat of solution, cal/g.	0.0718	Heat of solution, cal/g.	0.0718

Calorimeter used - 100 cc. glass calorimeter with 100 cc. standard cell.
Calorimeter used - 100 cc. glass calorimeter with 100 cc. standard cell.

The Potentiometer - Galvanometer
(Ammeter) meter (uv) reading
(scale div.)

Ammonia vaporized from
calorimeter during 15 min of
stirring temperature
equilibrated.
Gas-liquid system
residual
Ammonia remaining
1-50 ml. at 1-500.2 mm
with temperature 23 ± 0.1° C.

(minutes)	(uv)	(Scale div.)	Notes
35	1115.0	54.3	Barometer : 765.1 mm
36		54.2	
37		54.2	Cooling off
38		54.2	
39		54.1	Calorimeter line pressure
40		53.8	Manometer reading
41		53.7	L-828.3 mm R-792.8 mm
42		53.6	
43	1120.0	60.8	
44		60.7	Battery balanced; galvanometer rest point 46.6
45		60.6	
46		60.5	
47			Sample bulb crushed
48	1085.0	19.0	Reaction initiated
49	1100.0	35.0	
50		53.1	Great bubbling. Large
51		49.7	change in E.M.F.
52		49.7	
53		49.8	Needle valve opened
54		49.8	
55		49.8	Battery balanced: galvanometer rest point 46.5
56	1115.0	57.1	
57		57.1	
58		57.1	Calorimeter line pressure
59		57.1	Manometer reading
60		57.1	L-827.6 mm R-793.5 mm
61	1105.0	42.4	Ammonia vaporized during time of reaction.
			Gas-collecting system pressure
			Manometer reading
			L-660.7 mm R-995.2 mm
			Bath temperature 25.4 ± 0.1°C
			Ammonia vaporized from calorimeter during time of attaining temperature equilibrium.
			Gas-collecting system pressure:
			Manometer reading
			L-792.7 mm R-853.3 mm.
			Bath temperature 25.4 ± 0.1°C
			Barometer: 765.1 mm.

(minutes)	(psi)	(Scale div.)	Notes
35	1112.0	54.2	Barometer : 753.1 mm
36		54.2	
37		54.2	Cooling off
38		54.2	
39		54.1	Calorimeter line pressure
40		53.8	Manometer reading
41		53.7	I-828.5 mm R-792.5 mm
42		53.5	
43	1120.0	53.3	Battery balanced; battery-
44		53.2	meter test point 48.5
45		53.2	
46		53.2	Sample also obtained
47		53.0	Reaction initiated
48	1082.0	53.0	
49	1100.0	53.0	
50		52.1	Great bubbling. Large
51		49.7	change in ...
52		49.7	
53		48.8	Needle valve opened
54		48.8	
55		48.8	Battery balanced; battery-
56	1112.0	57.1	meter test point 48.5
57		57.1	
58		57.1	Calorimeter line pressure
59		57.1	Manometer reading
60		57.1	I-827.6 mm R-792.5 mm
61	1102.0	42.4	Ammonia vaporized during
			time of reaction.
			Gas-collecting vessel
			pressure
			Manometer reading
			I-828.7 mm R-792.5 mm
			Bar temperature 754.0.1°C

TABLE 10 EXPERIMENTAL DATA

DATE August 13, 1947
Determination of Heat
of Solution of Ammonium
Bromide in Ammonia

A. Wt. of NH_4Br sample

Wt. of bulb and NH_4Br	10.2355 g
Wt. of bulb	5.9446 g
Wt. of NH_4Br	4.2909 g
Vol. of bulb	3.92 ml.
Wt. of NH_4Br in vacuo	4.2909 g
Moles of NH_4Br	0.04379

B.

C. Wt. of NH_3 used in calorimeter.

Wt. of NH_3 and cylinder	709.43 g
Wt. of cylinder	597.42 g
Wt. of NH_3	112.01 g
Vol. of line	800 ml.
Wt. of NH_3 vapor in line	0.84 g
Wt. of NH_3 in calorimeter	117.17 g

D. Liquid Height in calorimeter

Cathetometer readings:

Bottom of liquid meniscus	749.2mm.
Reference mark	787.3mm.

Height of reference mark from bottom of calorimeter	176.7mm.
---	----------

Height of liquid from bottom	138.6mm.
------------------------------	----------

E. E.M.F. measurements

Potentiometer battery circuit
balanced with respect to standard cell.

Galvanometer rest point = 44.7 scale divisions

Time (minutes)	Potentiometer (uv)	Galvanometer reading (Scale div.)
-------------------	-----------------------	---

Notes

Ammonia vaporized from
calorimeter during time
of attaining temperature
equilibrium.

Gas-collecting system
pressure:

Manometer reading
L-792.7mm. R-665.5mm.

Bath temperature $25 \pm 0.1^\circ\text{C}$

Barometer: 762.8 mm.

(minutes)	(uv)	(Scale div.)	Notes
46	1120.0		Battery balanced; galvano-
47		50.3	meter rest point 44.5
48			
49		50.1	Calorimeter line pressure
50	1115.0	42.6	Manometer reading
51		42.5	L-816.9 mm R-785.4 mm
52		42.4	
53		42.3	
54		42.2	
55			At 56 sample bulb was
56		50.0	crushed.
56½	1088.0	48.8	Reaction initiated.
57			
58		36.8	
59		40.1	
60	1098.0	44.7	Battery balanced; galvano-
61	1108.0	51.3	meter rest point 44.5
62	1115.0	50.5	
63		50.2	Calorimeter line pressure
64		50.2	Manometer reading
65		50.2	L-816.5 mm R-785.5 mm
66		50.0	
67		49.8	
68		49.7	
69		49.5	Battery balanced; galvano-
70		49.4	meter rest point 44.6
71		49.2	
72		49.1	
73		49.9	Ammonia vaporized during
			time of reaction
			Gas-collecting system
			pressure
			Manometer reading
			L-665.8 mm R-855.8 mm
			Bath temperature $25 \pm 0.1^\circ\text{C}$

Latitudes	Longs	Local time	Notes
42	100.0	50.0	Battery exhausted; battery water test point 44.0
43		50.0	
44		50.0	
45		50.0	Colorimeter line pressure
46	100.0	50.0	Colorimeter reading
47		50.0	Colorimeter reading
48		50.0	Colorimeter reading
49		50.0	Colorimeter reading
50		50.0	Colorimeter reading
51		50.0	Colorimeter reading
52		50.0	Colorimeter reading
53		50.0	Colorimeter reading
54		50.0	Colorimeter reading
55		50.0	Colorimeter reading
56		50.0	Colorimeter reading
57		50.0	Colorimeter reading
58		50.0	Colorimeter reading
59		50.0	Colorimeter reading
60		50.0	Colorimeter reading
61		50.0	Colorimeter reading
62		50.0	Colorimeter reading
63		50.0	Colorimeter reading
64		50.0	Colorimeter reading
65		50.0	Colorimeter reading
66		50.0	Colorimeter reading
67		50.0	Colorimeter reading
68		50.0	Colorimeter reading
69		50.0	Colorimeter reading
70		50.0	Colorimeter reading
71		50.0	Colorimeter reading
72		50.0	Colorimeter reading
73		50.0	Colorimeter reading
74		50.0	Colorimeter reading
75		50.0	Colorimeter reading
76		50.0	Colorimeter reading
77		50.0	Colorimeter reading
78		50.0	Colorimeter reading
79		50.0	Colorimeter reading
80		50.0	Colorimeter reading
81		50.0	Colorimeter reading
82		50.0	Colorimeter reading
83		50.0	Colorimeter reading
84		50.0	Colorimeter reading
85		50.0	Colorimeter reading
86		50.0	Colorimeter reading
87		50.0	Colorimeter reading
88		50.0	Colorimeter reading
89		50.0	Colorimeter reading
90		50.0	Colorimeter reading
91		50.0	Colorimeter reading
92		50.0	Colorimeter reading
93		50.0	Colorimeter reading
94		50.0	Colorimeter reading
95		50.0	Colorimeter reading
96		50.0	Colorimeter reading
97		50.0	Colorimeter reading
98		50.0	Colorimeter reading
99		50.0	Colorimeter reading
100		50.0	Colorimeter reading

IV Calculations

The heat of reaction is calculated as the sum of the heat effect associated with the change in temperature of the calorimeter and contents and the heat absorbed in the vaporization of the amount of ammonia collected in the gas-collecting vessel. The change in temperature of the calorimeter (and contents) multiplied by the total heat capacity of the system yields the value of the heat effect producing the observed temperature change.

A. Calculation of the temperature change.

The temperature change is due to the sum of two factors, the heat removed or added to the calorimeter plus the heat leaking in or out through the walls of the calorimeter and any method for evaluation of the actual temperature change from the data must necessarily include these.

The very reliable method described by White¹³ is that adopted for the calculations in this research. The temperature pattern of the experiment is obtained by plotting as a function of time the thermocouple E.M.F.'s which are linearly related to temperatures for short temperature ranges and drawing through the resulting points a smooth curve. (See figures 10 through 17).

To the observed temperature change Δt (the difference between the final and initial temperatures of the reaction period) is added the temperature change η attributed to the thermal leakage of the calorimeter. This latter temperature change

13. White, W.P., The Modern Calorimeter, ACS, Monograph Series Chemical Catalogue Company, N.Y. 1928

IV. Calculations

The heat of reaction is calculated as the sum of the heat effect associated with the change in temperature of the calorimeter and the heat absorbed in the vaporization of the solvent of ammonia collected in the gas-collecting vessel. The change in temperature of the calorimeter (and contents) multiplied by the total heat capacity of the system yields the value of the heat effect involving the observed temperature

change.

A. Calculation of the temperature change.

The temperature change is due to the sum of two factors, the heat removed or added to the calorimeter plus the heat lost in or out through the walls of the calorimeter and any water. For evaluation of the actual temperature change from the data and necessarily include these.

The very reliable method described by White¹² is that adopted for the calculations in this research. The temperature history of the experiment is obtained by plotting as a function of time the thermocouple E.M.F.'s which are linearly related to the first few short temperature rises and dropping through the remaining values a smooth curve. (See Figure 10 through 17.)

To the observed temperature change ΔT (the difference between the final and initial temperatures of the reaction system) is added the temperature change ΔT_c attributed to the heat loss of the calorimeter. This latter temperature change

12. White, F. S., *Modern Calorimeter*, ACS, Monograph Series Chemical Catalogue Company, N.Y. 1933

FIG. 10. TEMPERATURE PATTERN EXPERIMENT C. LITHIUM

A. EVALUATION OF θ_x

TIME INTERVAL	MEAN EMF
27½-28½	1136.9 μ V
28½-29½	1152.3
29½-30½	1153.3
30½-31½	1153.8
31½-32½	1153.8
$\theta_x =$	1150.0 μ V

$$\begin{aligned}\theta_1 &= 1153.2 \\ \theta_2 &= 1121.6 \\ V_1 &= -0.22 \\ V_2 &= 0.28 \\ \Delta\theta &= 31.9\end{aligned}$$

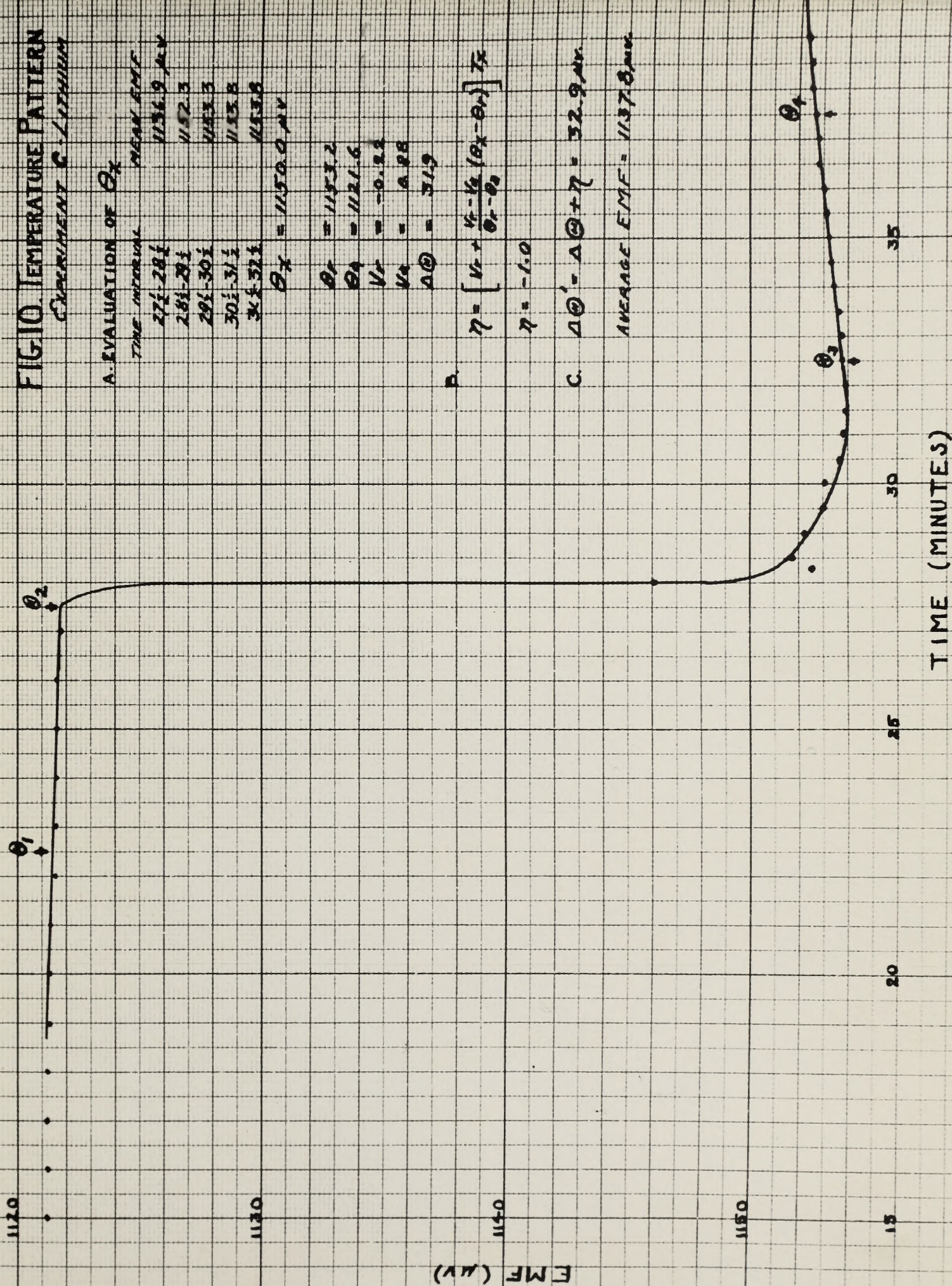
B.

$$\eta = \left[V_1 + \frac{V_2 - V_1}{\theta_1 - \theta_2} (\theta_x - \theta_1) \right] / \tau_x$$

$$\eta = -1.0$$

C. $\Delta\theta' = \Delta\theta + \eta = 32.9 \mu$

$$\text{AVERAGE EMF} = 1137.8 \mu$$



112.0

112.5

113.0

113.5

EMF (mv)

FIG. II TEMPERATURE PATTERN
EXPERIMENT C - LITHIUM

A. EVALUATION OF θ_x	TIME INTERVAL	MEAN EMF
	9-10	1122.5 mv
	10-11	1129.8
	11-12	1131.6
	12-13	1132.0
	13-14	1132.1
	14-15	1132.0

$$\theta_x = 1130.0$$

$$\theta_r = 1131.6$$

$$V_r = -0.125$$

$$\theta_x = 1120.8$$

$$V_x = 0.0$$

$$\Delta\theta = 11.2$$

$$\text{AVE. EMF} = 1126.5$$

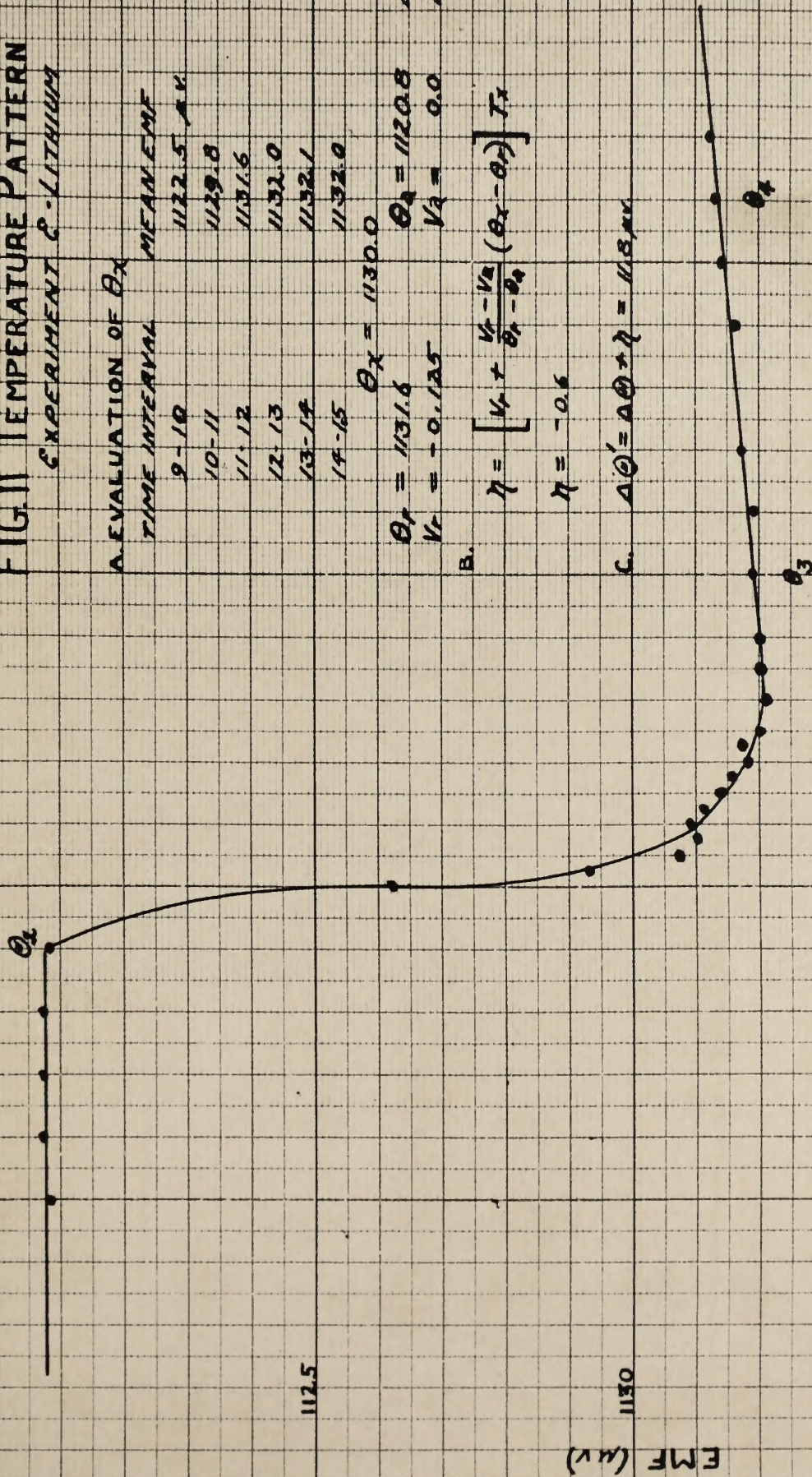
B.

$$\eta = \left[V_r + \frac{V_r - V_x}{\theta_r - \theta_x} (\theta_x - \theta_r) \right] T_x$$

$$\eta = -0.6$$

C.

$$\Delta\theta' = \Delta\theta + \eta = 11.8 \text{ mv}$$



TIME (MINUTES)

FIG. 12 TEMPERATURE PATTERN

EXPERIMENT F-LITHIUM

A. EVALUATION OF θ_x

TIME INTERVAL	MEAN EMF
39-40	1137.1
40-41	1145.1
41-42	1150.0
42-43	1151.6
43-44	1152.0
44-45	1152.3
45-46	1152.2

$$\begin{aligned}\theta_1 &= 1148.6 \\ \theta_2 &= 1151.5 \\ \theta_3 &= 1137.8 \\ V_1 &= -0.17 \\ V_2 &= 0.0 \\ \Delta\theta &= 17.3\end{aligned}$$

B.

$$\eta = \left[V_1 + \frac{V_1 - V_2}{\theta_2 - \theta_3} (\theta_2 - \theta_3) \right] T_x$$

$$\eta = -1.0$$

C.

$$\Delta\theta' = \Delta\theta + \eta = 18.3 \mu v$$

$$AVE. EMF = 1143.5 \mu v$$

EMF (mv)

TIME (MINUTES)

θ_2

θ_3

θ_4

FIG. 13 TEMPERATURE PATTERN EXPERIMENT G-LITHIUM

θ_2

θ_3

θ_1

EMF (μ V)

TIME (MINUTES)

A. EVALUATION OF θ_x
TIME INTERVAL MEAN EMF

37-38	1121.1
38-39	1135.4
39-40	1148.6
40-41	1151.2
41-42	1151.9
42-43	1152.3
43-44	1152.3

$$\theta_x = 1144.7$$

$$\begin{aligned}\theta_r &= 1151.7 \\ \theta_g &= 1120.4 \\ V_r &= -0.14 \\ V_g &= 0.03 \\ \Delta\theta &= 31.8\end{aligned}$$

B.

$$\eta = \left[V_r + \frac{V_r - V_g}{\theta_r - \theta_g} (\theta_x - \theta_r) \right] T_x$$

$$\eta = -0.7$$

$$C. \Delta\theta' = \Delta\theta + \eta = 32.5 \mu V$$

$$AVE. EMF = 1136.0 \mu V$$

35

40

45

50

55

60

1116

1126

1136

1146

FIG. 14. TEMPERATURE PATTERN

EXPERIMENT A - CESIUM

a. $\theta_x = 1157.1$
 $\theta_r = 1159.3$
 $\theta_s = 1128.3$
 $V_2 = 0.0$
 $V_r = -0.21$
 $\Delta\theta = 29.4$

b. $\eta = \left[\frac{V_r - V_s}{\theta_r - \theta_s} (\theta_x - \theta_r) \right] T_x$
 $\eta = -7.4$

c. $\Delta\theta' = \Delta\theta + \eta = 36.0 \mu V$
 AVE. E.M.F. = 1145.14V.

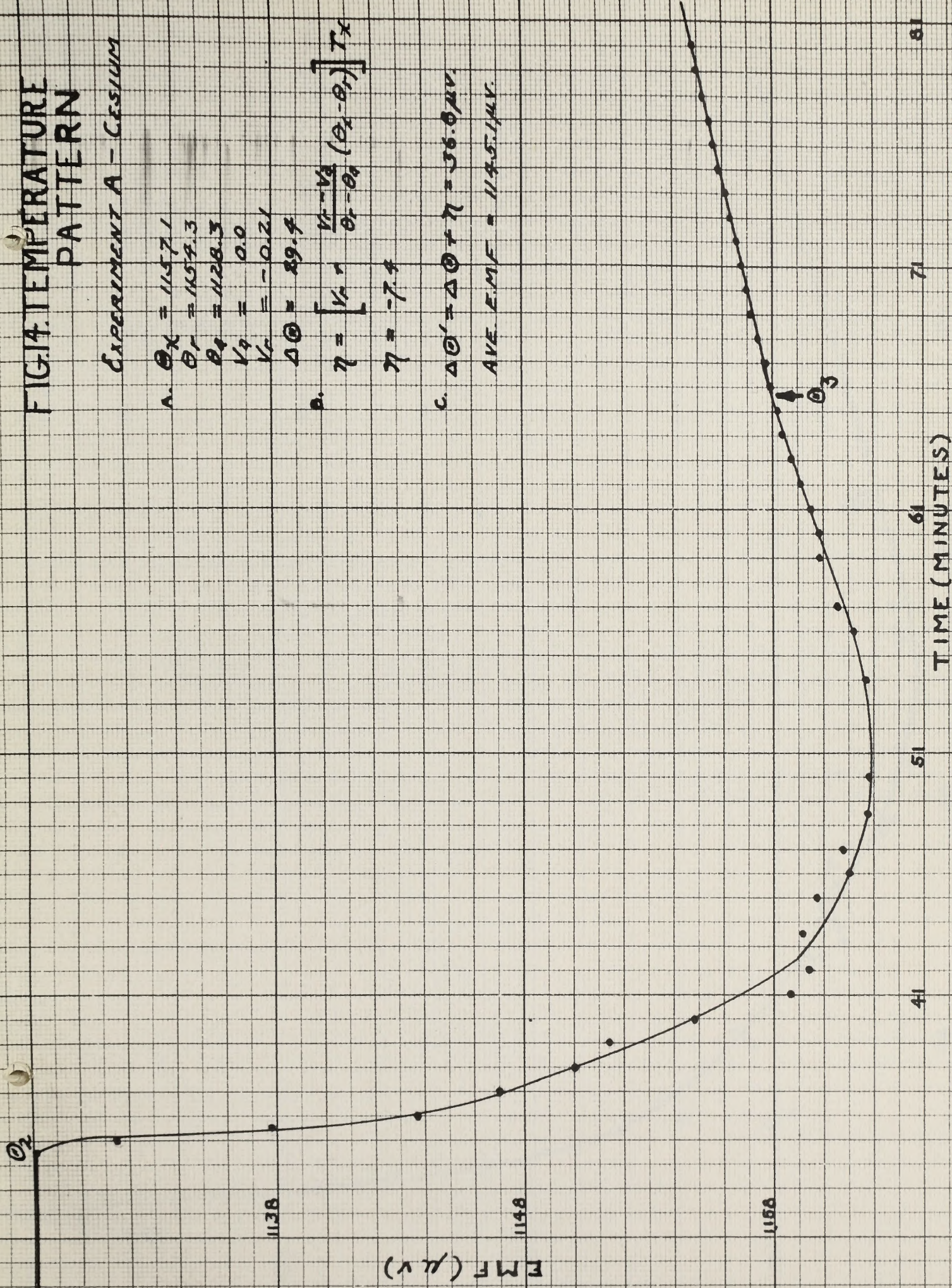


FIG. 15 TEMPERATURE PATTERN

EXPERIMENT C - Cesium

A

$$\begin{aligned}\theta_x &= 1140.8 \\ \theta_r &= 1141.3 \\ \theta_q &= 1114.6 \\ V_r &= -0.26 \\ V_q &= 0.0 \\ \Delta\theta &= 30.6\end{aligned}$$

B.

$$\eta = \left[V_r + \frac{V_r - V_q}{\theta_r - \theta_q} (\theta_x - \theta_r) \right] T_x$$

$$\eta = -7.65$$

C.

$$\Delta\theta' = \Delta\theta + \eta = 38.3 \mu V$$

$$\text{AVE. EMF} = 1130.2 \mu V$$

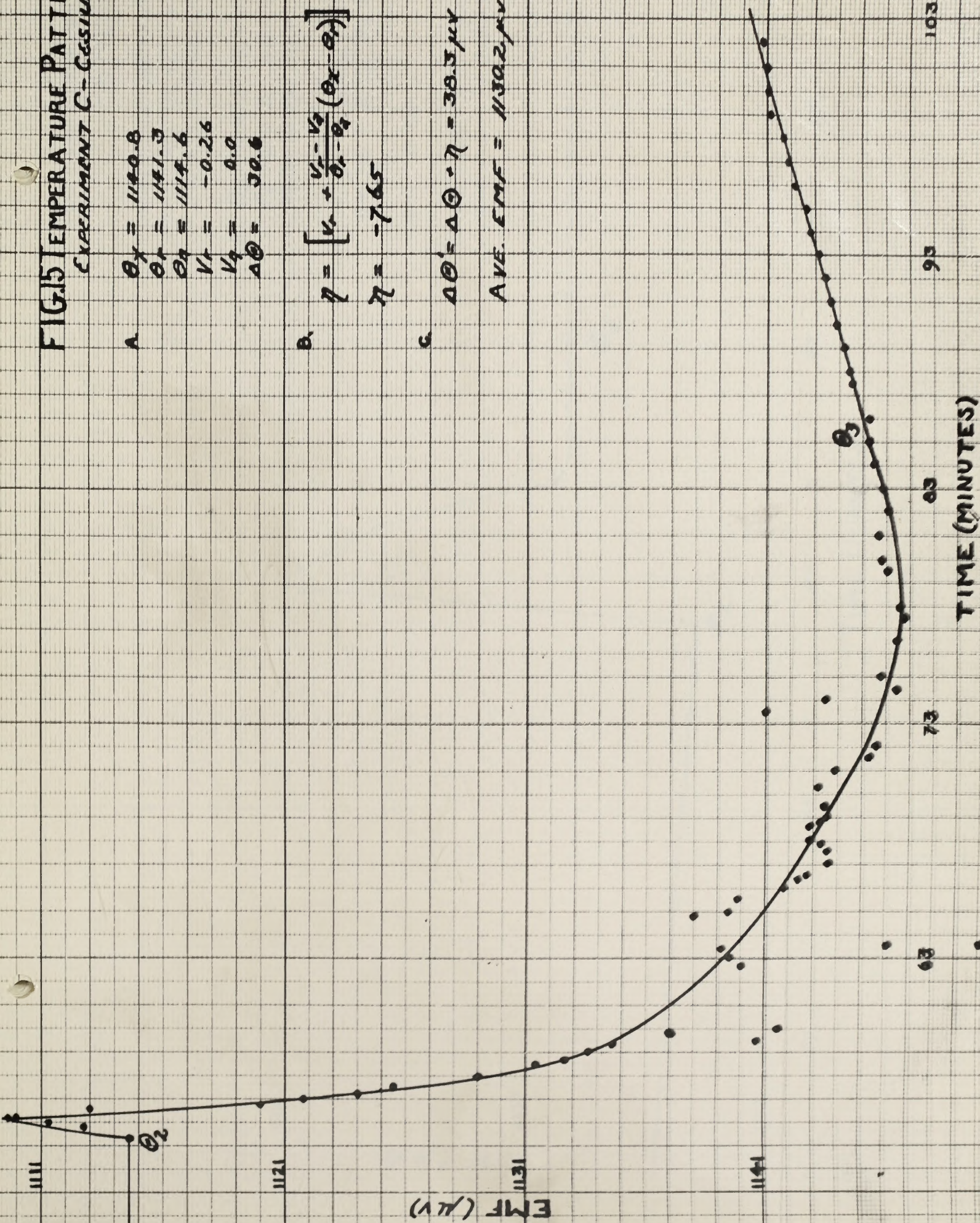


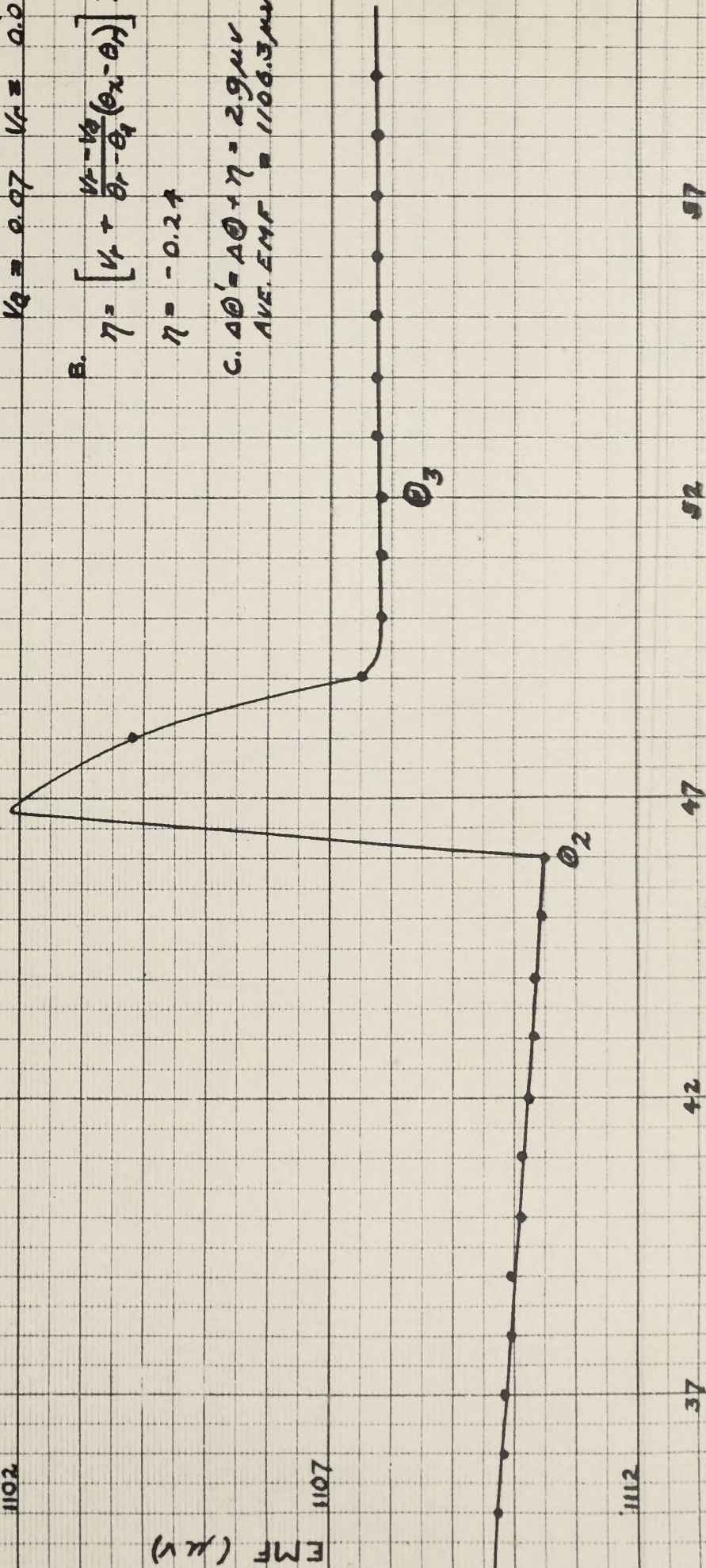
FIG. 6 TEMPERATURE PATTERN

EXPERIMENT: HEAT OF
SOLUTION OF LITHIUM
IN LIQUID AMMONIA

A. $\theta_x = 1106.2$ $\theta_r = 1107.7$
 $\theta_d = 110.3$ $\Delta\theta = -2.7$
 $V_d = 0.07$ $V_r = 0.0$

B. $\eta = \left[V_r + \frac{V_r - V_d}{\theta_r - \theta_d} (\theta_x - \theta_r) \right] T_x$
 $\eta = -0.24$

C. $\Delta\theta' = \Delta\theta + \eta = 2.9 \mu V$
 AVE. EMF = 1106.3 mV



TIME (MINUTES)

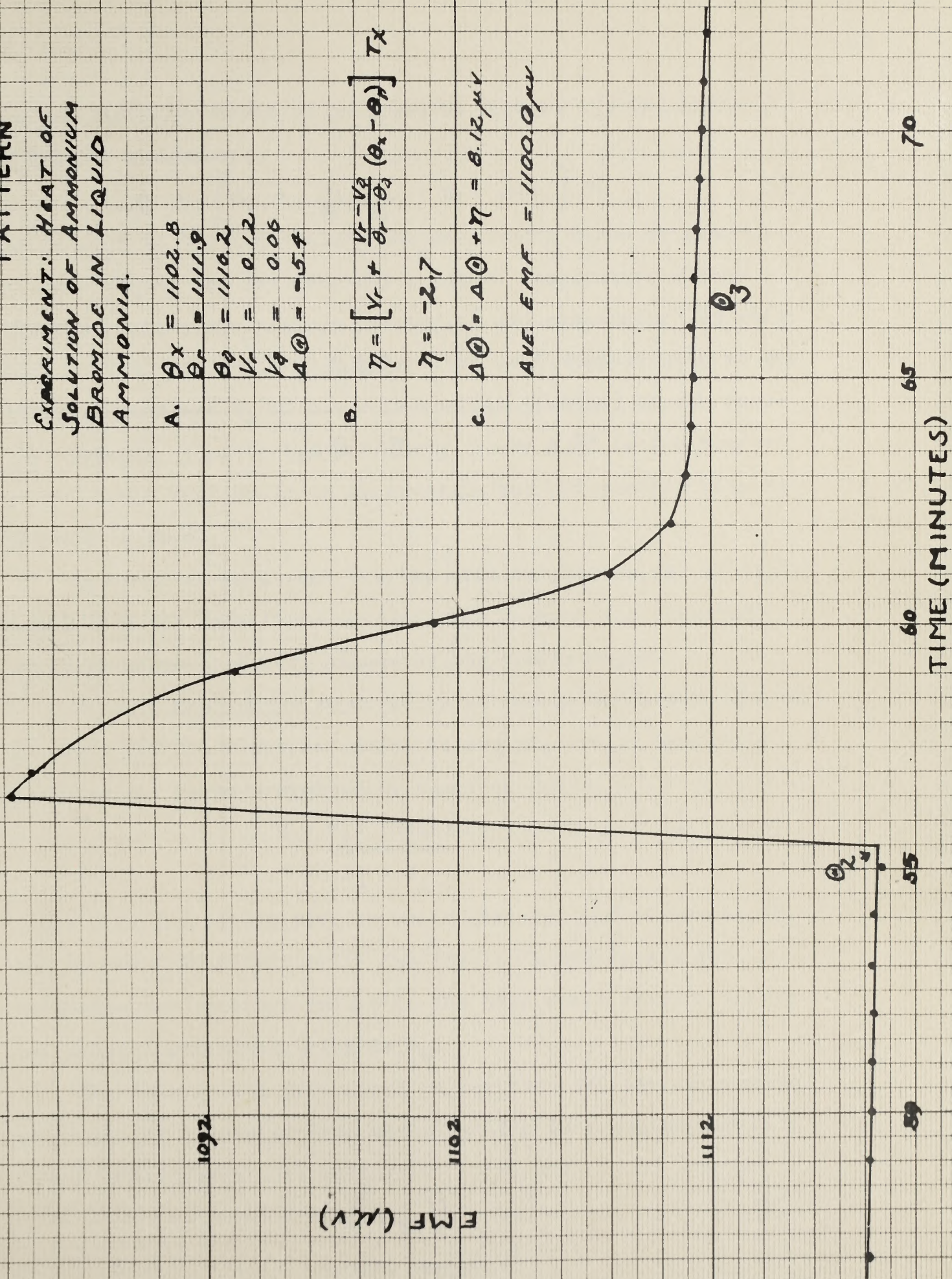
FIG. 17 TEMPERATURE
PATTERN

EXPERIMENT: HEAT OF
SOLUTION OF AMMONIUM
BROMIDE IN LIQUID
AMMONIA.

A. $\theta_x = 1102.8$
 $\theta_F = 1111.9$
 $\theta_0 = 1116.2$
 $V_1 = 0.12$
 $V_2 = 0.06$
 $\Delta\theta = -5.4$

B. $\eta = \left[V_1 + \frac{V_1 - V_2}{\theta_1 - \theta_2} (\theta_x - \theta_1) \right] T_x$
 $\eta = -2.7$

C. $\Delta\theta' = \Delta\theta + \eta = 8.12 \mu v$
 AVE. EMF = 1100.0 μv



is calculated by means of an improved form of the Regnault-Pfaundler equation:

$$\eta = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_q} (\theta_x - \theta_r) \right] T_x \quad (5)$$

in which η is the temperature change brought about by thermal leakage, V_a, V_r are the constant rates of temperature change observed during the periods preceeding and succeeding the reaction period, respectively, $\theta_q, \theta_x, \theta_r$ are the mean temperatures of the three periods and T_x is the duration (in minutes) of the reaction period. Therefore, $\Delta \Theta' = \Delta \Theta + \eta$, where $\Delta \Theta'$ is the temperature change that would be produced in the calorimeter with no thermal leakage.

In order to construct the temperature pattern for an experiment from the data it is necessary to convert the observed scale readings to E.M.F. values of the thermocouple.

By determining the sensitivity of the galvanometer (number of scale divisions corresponding to one microvolt) the scale readings may be so converted by equation (6).

$$S = \frac{R_B - (R_A + \Delta R)}{P_B - P_A} \quad (6)$$

where S is the sensitivity in scale division per microvolt, R_A and R_B are consecutive scale readings. P_A and P_B are the potentiometer settings and ΔR is the mean scale reading change per minute determined prior to R_A .

The sensitivity determined in equation (6) is now used in equation (7) to change each scale reading to a corresponding E.M.F. value, E in microvolts:

$$E = P + \left(\frac{R_0 - R}{S} \right) \quad (7)$$

is obtained by means of an improved form of the apparatus.

Receptor equation:

$$(2) \quad \gamma = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a} (\theta_r - \theta_a) \right] T_x$$

in which γ is the temperature change, V_r and V_a are the constant rates of temperature change

observed during the periods preceding and succeeding the reaction period, respectively, θ_r and θ_a are the mean temperatures of the reaction periods and T_x is the reaction (in minutes) of the reaction period. Therefore, $\Delta\theta = \Delta\theta_r + \Delta\theta_a$, where $\Delta\theta_r$ is the temperature change that would be produced in the calorimeter with no thermal leakage.

In order to construct the temperature pattern for an experiment from the data it is necessary to convert the observed

scale readings to A.M.U. values of the thermocouple.

To determine the sensitivity of the galvanometer (number

of scale divisions corresponding to one microvolt) the scale

reading is to be converted by equation (3).

$$(3) \quad \mu = \frac{R_2 - (R_1 + \Delta R)}{R_2 - R_1}$$

where μ is the sensitivity in scale divisions per microvolt, R_1

and R_2 are consecutive scale readings, ΔR and μ are the

potential meter settings and ΔR is the mean scale reading change

per minute determined prior to R_1 .

The sensitivity determined in equation (3) is now used in

equation (7) to change each scale reading to a corresponding

A.M.U. value, θ is microvolts:

$$(7) \quad \theta = \mu (R - R_1)$$

P is the setting of the potentiometer, R_0 is the scale reading of the galvanometer with the circuit open, R is the scale reading, and S is the sensitivity.

Since values of E are used in the place of temperatures in applying the method of determining ΔH to the temperature pattern, ΔH calculated in this way is expressed in microvolts. To find the equivalent of this in degrees centigrade, ΔH in microvolts is divided by the value of dE/dT determined from table 30 in the appendix, for the mean E.M.F. of the reaction period.

B. Calculation of the Heat Capacity of the Calorimeter and Contents.

The calorimetric method requires a knowledge of the heat capacity of all parts of the system that undergo the temperature change calculated. The system includes the liquid ammonia and dissolved ammonium salt, the alkali metal sample in the bulb, the platinum stirrup and gauze, and all glass that is in contact with the liquid (the calorimeter walls, submerged portions of the stirrer, thermocouple well and sample-bulb rod and the sample-bulb).

The heat capacity of the platinum and minor glass parts is readily calculated by multiplying the respective values of the specific heat by the weights of each involved.

The heat capacity of the glass walls of the calorimeter in contact with the liquid ammonia varies linearly with the height of the liquid level. Determinations of the heat capacity of the calorimeter as a function of liquid level height is described in the appendix, the results of which indicate the linearity of

is the reading of the calorimeter, Δ_0 is the scale reading of the calorimeter with the circuit open, Δ is the scale reading, and Δ_0 is the sensitivity.

Since values of Δ are used in the place of Δ_0 in the calculation of the heat of reaction, Δ_0 to the temperature correction, Δ_0 calculated in this way is expressed in microvolts. The line the equivalent of this in terms of microvolts, Δ_0 in microvolts is divided by the value of Δ_0 determined from Table 30 in the appendix, for the mean Δ_0 of the reaction series.

3. Calculation of the heat capacity of the calorimeter and contents.

The calorimetric method requires a knowledge of the heat capacity of all parts of the system that undergo the temperature change calculated. The system includes the liquid ammonia and dissolved sodium salt, the silver metal seal in the bulb, the platinum stirrer and gauge, and all glass that is in contact with the liquid (the calorimeter walls, submerged portions of the stirrer, thermocouple well and sample-bulb rod and the sample-bulb).

The heat capacity of the platinum and minor glass parts is readily calculated by multiplying the respective values of the specific heat by the weights of each involved.

The heat capacity of the glass walls of the calorimeter in contact with the liquid ammonia varies linearly with the height of the liquid level. Description of the heat capacity of the calorimeter as a function of liquid level height is described in the appendix, the results of which indicate the linearity of

the variation. The liquid level in the calorimeter is calculated from the cathetometer readings, for the meniscus and reference mark which is a known distance from the bottom of the calorimeter. For any particular liquid level thus calculated the corresponding value of the heat capacity of the calorimeter is obtained by reference to figure 20 in the appendix.

The heat capacity of the liquid ammonia is obtained as the product of the specific heat of the ammonia and the quantity in the calorimeter. Values of the specific heat for a small range of temperatures around the boiling point of liquid ammonia are given in table 11.¹⁴ (See below) The value of the specific heat corresponding to the mean temperature of the reaction period is that used.

TABLE 11

HEAT CAPACITY OF LIQUID AMMONIA

$T^{\circ} \text{K}$	C_p (Cal./mole/ $^{\circ}\text{T}$)
229.93	18.02
233.15	18.05
234.76	18.05
238.33	18.12
239.68	
240.5	18.16
Interpolated:	
	(Calculated specific heat) (cal/g/ $^{\circ}\text{C}$)
239.1 (-34°C)	18.14 1.065
240.1 (-33°C)	18.13 1.065
241.1 (-32°C)	18.12 1.064

The weight of ammonia in the calorimeter which is involved in the temperature change associated with the reaction is

14. Overstreet and Giauque, J. Am. Chem. Soc., 59, 254 (1937)

the variation. The liquid level in the calorimeter is calculated from the calorimeter readings. For the meniscus and reference mark which is a known distance from the bottom of the calorimeter. For any particular liquid level thus calculated the corresponding value of the heat capacity of the calorimeter is obtained by reference to Figure 20 in the appendix.

The heat capacity of the liquid ammonia is obtained as the product of the specific heat of the ammonia and the density in the calorimeter. Values of the specific heat for a small range of temperatures around the boiling point of liquid ammonia are given in Table II. (See below) The value of the specific heat corresponding to the mean temperature of the reaction period is that used.

TABLE II

HEAT CAPACITY OF LIQUID AMMONIA

C_p (Cal./mole/°C)	T (°C)
18.02	239.93
18.05	239.15
18.05	238.78
18.12	238.53
18.12	238.68
18.12	240.8

Interpolated:	
239.1 (-34°C)	18.14
240.1 (-33°C)	18.15
241.1 (-32°C)	18.12

Calculated specific heat (cal./mole/°C)	
1.088	18.14
1.088	18.15
1.084	18.12

The weight of ammonia in the calorimeter which is involved in the temperature change associated with the reaction is

14. Overstreet and Stanger, J. Am. Chem. Soc., 59, 284 (1937)

calculated from the weight condensed in the calorimeter by subtracting the weight vaporized while reaching temperature equilibrium before the reaction and by subtracting one half the weight vaporized in the course of the reaction. This weight is calculated as shown.

These various heat capacities described when summed equal the heat capacity of the system undergoing the calculated temperature change.

C. Calculation of the molar heat effect.

The product of ΔT and the total heat capacity of the system yields the value of the heat extracted from or absorbed by the calorimeter and contents. This quantity of heat which produces ΔT is equal to the sum of the quantity of heat removed from the calorimeter by the vaporized ammonia and that quantity evolved in the reaction of the alkali metal with the ammonium ion.

The weight of ammonia vaporized multiplied by the heat of vaporization per gram at the mean temperature of the reaction period equals the heat removed from the calorimeter on vaporization. Table 12¹⁵ gives values of the heat of vaporization at corresponding temperatures.

TABLE 12
HEAT OF VAPORIZATION OF LIQUID AMMONIA

Data from Ref. 15

Interpolated values

T°C	H (joules)	T°C	H (cal/g)
-35.0	1373	-34	327.6
-33.4	1369	-33	326.9
-30.0	1359	-32	326.2
-25.0	1344	-31	325.5

15. Osborne and Van Dusen, Bur.Stand.Bull. 14, 439 (1917)

or J.Am.Chem.Soc. 40, 14 (1918), J.Am.Chem.Soc., 52, 757 (1930)

The weight of ammonia vaporized and collected in the gas-collecting vessel is calculated by use of Berthelot's equation of state which on substitution of the critical values¹⁶ assumes the form of equation (8):

$$g = \frac{P V}{1 - 0.00828 P} (0.006964) \quad (8)$$

Where g is the weight in grams of ammonia, P is the pressure in atmospheres of the ammonia as indicated by the manometer of the gas-collecting system and V is the volume in milliliters of ammonia gas collected. Since both hydrogen and ammonia gases are evolved, in the course of the reaction, assuming Dalton's Law of Partial Pressure, the volume of ammonia collected is equal to the volume of the gas-collecting system, 6715 milliliters, less the volume of hydrogen. This latter volume is calculated from the ideal gas law, $P V = n R T$, assuming hydrogen to approximate an ideal gas. The number of moles of hydrogen evolved is one half the number of gram-atoms of alkali metal reacting.

A correction to the weight of ammonia collected must be included here for any change in calorimeter line pressure before and after the reaction. The weight of ammonia in the line at each pressure is calculated by use of the equation of state mentioned above, in which is substituted the volume of the line. This volume, 900 milliliters, is that of all glass line plus one half the volume of the calorimeter above the liquid level. This latter estimation takes into account the temperature gradient from room temperature to liquid ammonia temperature in the

16. Giauque and Overstreet, J. Am. Chem. Soc., 59, 757 (1937)

calorimeter. The difference in the weight of ammonia in the line before and after the reaction is added to the weight vaporized.

The heat evolved in the reaction of the given sample weight plus the quantity of heat removed by the ammonia vaporized during the reaction (a negative quantity) equals the quantity of heat producing the observed ΔT . Dividing the heat evolved in the reaction by the number of gram-atoms of alkali metal that has reacted yields heat evolved per gram-atom of metal, ΔH_1 .

The calculations for one experiment are presented in detail in table 13, and summaries of the calculations for each experiment are shown in tables 14 - 21.

NOTE:

The values of ΔH_1 and ΔH_2 measured for lithium are corrected for the impurities contained in the lithium metal (See Table 1). From the following detailed considerations, the correction factor 0.995 for the heat of solution of lithium is calculated. Dividing the measured value of ΔH_2 by this factor yields a ΔH_2 value corrected for impurities in the sample.

From similar considerations as shown below, the correction factor results by which values of ΔH_1 are then corrected upon division by this factor.

The correction factor to be applied to ΔH_2 , the heat of solution of lithium is arrived at by considering the number of equivalents represented by one gram-atom of the impure sample upon which basis the ΔH_2 is calculated from the measurements:

calorimeter. The difference in the weight of ammonia in the line before and after the reaction is added to the weight variation. The heat evolved in the reaction of the given sample weight plus the quantity of heat removed by the ammonia vaporized during the reaction (a negative quantity) equals the quantity of heat evolved in the observed ΔH . Dividing the heat evolved in the reaction by the number of gram-atoms of lithium metal that reacted yields heat evolved per gram-atom of metal, ΔH_1 . The calculations for one experiment are presented in detail in Table 13, and summaries of the calculations for each experiment are shown in Tables 14 - 21.

NOTES:

The values of ΔH_1 and ΔH_2 measured for lithium are corrected for the two effects contained in the lithium metal (see Table 1). From the following detailed consideration, the correction factor 0.993 for the heat of solution of lithium is calculated. Dividing the measured value of ΔH_2 by this factor yields a ΔH_2 value corrected for impurities in the sample. From the following considerations as shown below, the correction factor 0.993 results of which values of ΔH_1 are then corrected upon division by this factor. The correction factor to be applied to ΔH_2 , the heat of solution of lithium is arrived at by considering the number of equivalents represented by one gram-atom of the impure sample upon which basis the ΔH_2 is calculated from the measurements:

Equivalents assumed to be present	Equivalents (in terms of Li) actually present
---	---

1 gram-atom Li sample
or 6.940 grams consists of:

Lithium (0.9947 gram-atoms)	1	0.9947
Calcium (0.0002 gram-atoms)		0.0002
Sodium (0.0005 gram-atoms)		-0.0001
Potassium (0.0001 gram-atoms)		0.0000
	<u>1</u>	<u>0.9948</u>

Therefore, the correction factor is 0.995

The correction factor to be applied to the values of ΔH_1 for lithium is found similarly:

Equivalents assumed to be present	Equivalents actually present
---	---------------------------------

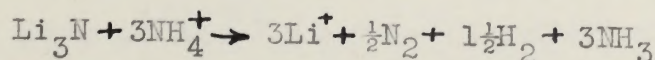
1 gram-atom Li sample
or 6.940 grams consists of:

Lithium (0.9947 gram-atoms)	1	0.9947
Calcium (0.0002 gram-atoms)		0.0004
Sodium (0.0005 gram-atoms)		0.0004
Potassium (0.0001 gram-atoms)		0.0001
	<u>1</u>	<u>0.9956</u>

Thus the correction factor 0.996 divided into values of ΔH_1 will yield corrected values as tabulated in table 22 and 23.

The heat content of nitrogen (present as an impurity to the extent of 0.15% by weight) probably in the form of Li_3N is probably close to the heat content of the products of the reaction, Li , N_2 , NH_3 and H_2 . Therefore, nitrogen may be considered as an inert impurity.

Or from another point of view, each gram-atom of nitrogen is 3 equivalents for the reaction:



Equivalent is assumed to be (in terms of H₂) actually present

I gram-atom of sample or 8.940 grams consists of:

0.9947	1	Lithium (0.9947 gram-atom)
0.0003		Calcium (0.0003 gram-atom)
-0.0001		Sodium (0.0003 gram-atom)
0.0000		Potassium (0.0001 gram-atom)
0.9943	1	

Therefore, the correction factor is 0.993

The correction factor to be applied to the values obtained for

lithium is found similarly:

Equivalent is assumed to be actually present

I gram-atom of sample or 8.940 grams consists of:

0.9947	1	Lithium (0.9947 gram-atom)
0.0004		Calcium (0.0003 gram-atom)
0.0004		Sodium (0.0003 gram-atom)
0.0001		Potassium (0.0001 gram-atom)
0.9956	1	

Thus the correction factor 0.993 divided into values obtained

will yield corrected values as tabulated in Table 22 and 23.

The heat content of nitrogen (present as an impurity in the

extent of 0.1% by weight) probably in the form of H₂ is

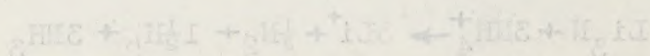
probably close to the heat content of the products of the reac-

tion, Li, Na, K, and H₂. Therefore, nitrogen may be considered

as an inert impurity.

Or from another point of view, each gram-atom of nitrogen

is 3 equivalents for the reaction:



and since the equivalent weight of lithium, 6.9 grams and that of nitrogen, 4.7 grams, are of the same order of magnitude and assuming the heat of the above reaction and that of the solvated electron with the ammonium ion to be approximately the same, one may consider nitrogen in its effect to be inert

at $T = 45 \text{ min}$:

$$R = \frac{49.3 - (55.7 \times 2.3)}{1149 - 1153}$$

$$S = 1.58 \text{ scale div/v}$$

Using equation (7):

$$E = P + \frac{R_0 - R}{S} \quad (7)$$

$$E = 1121.0 \frac{(51.6 - 51.6)}{1.58} = 1121.0$$

Continued substitution into equation (7) of values of P, R, R_0 and S result in corresponding values of E which are tabulated as shown:

Time	P	R	E (mv)
0	1121.0	51.6	1121.0
1	1121.0	51.58	1121.0
2	1121.0	51.55	1121.0
3	1121.0	51.48	1121.1

where P equals potentiometer settings in micro volts, R equals observed scale readings and E equals calculated E.E.F.'s in micro volts. These values of E are then plotted as in figure 10.

Calculations of $\Delta\theta$ are shown in figure 10, where the modified form of the Regener-Transfer equation is used. $\Delta\theta$ is now changed to $\Delta\theta$ in degrees centigrade:

and since the equivalent weight of nitrogen is 14.0 grams and that of hydrogen, 1.0 gram, are of the same order of magnitude as the weight of the gas, the weight of the gas is approximately the same as the weight of the gas. The weight of the gas is approximately the same as the weight of the gas. The weight of the gas is approximately the same as the weight of the gas.

TABLE 13
SAMPLE OF CALCULATIONS OF THE HEAT
OF REACTION ΔH_1 FOR EXPERIMENT C (LITHIUM)

A. TEMPERATURE CHANGE

1. Temperature pattern

$$S = \frac{R_B - (R_A + \Delta R)}{P_B - P_A} \quad (6)$$

at T = 48 min:

$$S = \frac{49.3 - (56.9 + 0.3)}{1149 - 1154}$$

$$S = 1.58 \text{ scale div/uv}$$

Using equation (7):

$$E = P + \frac{R_0 - R}{S} \quad (7)$$

$$E = 1121.0 + \frac{(51.6 - 51.6)}{1.58} = 1121.0$$

Continued substitution into equation (7) of values of P, R, R_0 and S result in corresponding values of E which are tabulated as shown:

<u>Time</u>	<u>P</u>	<u>R</u>	<u>E (uv)</u>
0	1121.0	51.6	1121.0
1	1121.0	51.65	1121.0
2	1121.0	51.55	1121.0
3	1121.0	51.45	1121.1

where P equals potentiometer settings in micro volts, R equals observed scale readings and E equals calculated E.M.F.'s in micro volts. These values of E are then plotted as in figure 10.

Calculations of $\Delta \theta$ are shown in figure 10, where the modified form of the Regnault-Pfaundler equation is used. $\Delta \theta$ is now changed to ΔT in degrees centigrade:

TABLE 13
EFFECT OF CHANGING TEMPERATURE ON THE RATE
OF REACTION ΔH FOR EXPERIMENT 6 (CONTINUED)

TEMPERATURE CHANGE

TEMPERATURE DEGREE

(6)

$$S = \frac{R - (R + \Delta R)}{T - T_0}$$

$$S = \frac{49.3 - (58.9 + 0.3)}{11.49 - 11.84} \quad \text{at } T = 48 \text{ min.}$$

$$S = 1.58 \text{ sec/deg}$$

Using equation (7):

(7)

$$S = \frac{R_0 - R}{T}$$

$$S = \frac{11.0 - 11.8}{1.58} = -0.51$$

Continued substitution into equation (7) of values of R, R_0 and S result in corresponding values of T which are tabulated as shown:

Time	S	R	T (deg)
0	11.0	51.8	11.0
1	11.0	51.85	11.0
2	11.0	51.85	11.0
3	11.0	51.45	11.1

where S equals potentiometer reading in micro volts, R equals observed emf reading and T equals calculated $E.M.F.$'s in micro volts. These values of T are then plotted as in figure 10.

Calculations of ΔH are shown in figure 10, where the modified form of the van't Hoff equation is used. ΔH is now changed to ΔT in degrees centigrade:

$$\Delta H' = 32.9 \text{ uv}$$

$$\text{Average } E = 1137.8 \text{ uv}$$

$$\Delta T = \frac{\Delta H'}{dE/dT} = - \frac{32.9}{32.65} = -1.01^\circ \text{ C}$$

B. HEAT CAPACITY OF SYSTEM

(Calculations indicated in table 14)

Ammonia vaporized prior to reaction:

$$g = \frac{P V}{1 - 0.00828 P} (0.0006964) \quad (8)$$

$$P = (795.9 \text{ mm} - 516.0 \text{ mm})/760$$

$$g = \frac{\frac{279.9}{760} \times 6715 \times 0.0006964}{1 - 0.00828 \times \frac{279.9}{760}} = 1.73$$

The respective heat capacities of all parts of the system involved in the temperature change are summed to give the total heat capacity of the system.

C. HEAT EFFECT

1. Moles of hydrogen evolved = $\frac{1}{2}$ gram-atoms of Li =

$$\frac{1}{2} (0.00615) = 0.00308$$

2. Volume of hydrogen evolved

$$P V = n R T$$

Gas-collecting system pressure:

Manometer readings

$$427.8 \text{ mm}$$

$$240.8 \text{ mm}$$

$$232.0 \text{ mm}$$

$$P = \frac{232}{760} \text{ atmospheres}$$

$$T = 298^\circ \text{K}$$

$$V = \frac{nRT}{P} = \frac{0.00308 \times 82.05 \times 298}{232.0/760}$$

$$V = 247 \text{ ml}$$

3. Volume of NH_3 evolved (See next page)

Vol. of Gas-collecting system	6715 ml
Vol. of Hydrogen	-247 ml
Vol. of NH_3 vaporized	6468 ml

4. Weight of NH_3 evolved

$$g = \frac{P V}{1 - 0.00828 P} = 0.0006964 \quad (8)$$

$$P = 232.0/760$$

$$V = 6468$$

$$g = \frac{(232.0/760) (6468) (0.0006964)}{1 - 0.00828 (232.0/760)}$$

$$g = 1.379 \text{ g}$$

5. Correction for change in calorimeter line pressure before

and after: Using equation (8) before reaction, $P =$

$(31.5/760)$, $V = 900 \text{ ml.}$; after reaction, $P =$
 $(33.5/760)$, $V = 900 \text{ ml.}$ The increase in g is the

additional amount of ammonia vaporized to increase the
 line pressure. A rough estimate is 1 mg. ammonia per
 1 mm. increase in line pressure.

The heat producing the observed temperature change of the
 calorimeter and contents is found by multiplying the temperature
 change observed, -1.01°C by the heat capacity of the system,
 137.8. Since ΔT represented a decrease in temperature, heat
 was removed from the system and $\Delta T \times \text{Heat Capacity} = -139 \text{ cal-}$
 ories.

The heat removed from the calorimeter and contents by the
 vaporization of the calculated amount of ammonia is evaluated
 by multiplying together this weight of ammonia in grams and
 the heat of vaporization per gram at the mean temperature of
 the calorimeter. Thus, $1.381 \text{ g.} \times 327 \text{ cal/g.}$ indicates that

Vol. of gas collected system 2715 ml
Vol. of hydrogen 234 ml
Vol. of air vaporized 2483 ml

4. Volume of H₂ evolved

$$e = \frac{V}{I - 0.00828 P} = \frac{234.0 \sqrt{760}}{1 - 0.00828 (234.0 \sqrt{760})} = 2483 \text{ ml}$$

$$e = 1.279 \text{ g}$$

5. Correction for change in calorimeter line pressure before and after: Using equation (8) before reaction, $P = 234.0 \sqrt{760}$, $V = 900 \text{ ml}$; after reaction, $P = 2483 \sqrt{760}$, $V = 900 \text{ ml}$. The increase in e is the additional amount of ammonia vaporized to increase the line pressure. A rough estimate is 1 mg. ammonia per 1 mm. increase in line pressure.

The heat produced, the observed temperature change of the calorimeter and contents is found by multiplying the temperature change observed, -1.01°C by the heat capacity of the system, 137.8. ΔT represented a decrease in temperature, heat was removed from the system and $\Delta T \times \text{Heat Capacity} = -139 \text{ cal}$.

The heat removed from the calorimeter and contents by the vaporization of the calculated amount of ammonia is evaluated by multiplying this weight of ammonia in grams and the heat of vaporization per gram at the mean temperature of the calorimeter. Thus, $1.381 \text{ g} \times 329 \text{ cal/g}$ indicates that

452 calories are removed. This amount of heat is written -452 cal.

By use of the expression advanced previously (quantity of heat evolved in the reaction of the given weight of sample plus quantity of heat removed by vaporization of ammonia (this value being given a negative sign to indicate heat being removed from the calorimeter) equals quantity of heat producing the observed temperature change, ΔT , in the calorimeter), the quantity of heat evolved in the reaction is calculated:

$$q(\text{calories of heat} + (-452 \text{ cal.}) = -139 \text{ cal.} \\ \text{evolved by the} \\ \text{reaction})$$

$$q \text{ calories of heat} = 313 \text{ calories} \\ \text{evolved by the} \\ \text{reaction}$$

ΔH_1 follows immediately,

$$\Delta H_1 = \frac{q \text{ evolved}}{\text{number of gram-atoms} \\ \text{of sample}} = \frac{313}{0.00615} = -50.9 \text{ Kcal}$$

In keeping with accepted conventions of thermochemistry, the value of ΔH_1 , for an exothermic reaction, is actually a negative quantity, and the minus sign is affixed to these values accordingly.

all calories are removed. This amount of heat is written -522 cal.

By use of the experimentally determined previously (quantity of heat evolved in the reaction of the given weight of sample plus quantity of heat removed by vaporization of ammonia) this value being given a negative sign to indicate heat being removed from the calorimeter) equals quantity of heat produced the observed temperature change, ΔT , in the calorimeter, the quantity of heat evolved in the reaction is calculated:

$$q \text{ calories of heat} + (-522 \text{ cal.}) = -132 \text{ cal.}$$

evolved by the
reaction

$$q \text{ calories of heat} = 513 \text{ calories}$$

evolved by the
reaction

ΔH follows immediately.

$$\Delta H = \frac{q \text{ evolved}}{\text{number of gram-atoms of sample}} = \frac{513}{0.00313} = -164,217 \text{ Kcal}$$

In keeping with accepted conventions of thermochemistry, the value of ΔH , for an exothermic reaction, is actually a negative quantity, and the minus sign is affixed to these values accordingly.

TABLE 14 SUMMARY OF CALCULATIONS FOR
EXPERIMENT C
(LITHIUM)

A. Temperature change

Average E (from temperature pattern)	1137.8 uv
Average T (Table 30)	-33.27°C
dE/dT (Table 30)	-32.65 uv/°C
$\Delta E(\Delta T)$	32.9 uv
ΔT	-1.01°C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat (Cal/g/°C)	Heat Capacity (Cal/°C)
1. NH ₄ Br	0.6271	0.21	0.1
2. Glass (Bulb, stirrer etc.)	2.5	0.2	0.5
3. Lithium	0.0426	0.7	0.0
4. Platinum	6.4	0.03	0.2
5. Calorimeter (From figure 20 for liquid height of 138.9 mm.			19.6
6. Ammonia in calorimeter:			
Weighed in	112.62		
Vaporized prior to reaction	1.73		
½ amount vaporized during reaction	0.69	1.065	117.4
Total for (6)	110.20		

Total Heat Capacity of System 137.8

C. Heat Effect

1. $\Delta T \times$ Heat capacity of system = -1.01 x 137.8 -139
2. Heat of vaporization:
 - a. Volume of gas-collecting system at 25°C
6715
 - b. Moles of H₂ evolved 0.00308
 - c. Volume of H₂ evolved
@ 232 mm, 25°C 247
 - d. Volume of NH₃ evolved
@ 232 mm, 25°C 6468
 - e. Wt. of NH₃ vaporized 1.379 g
line pressure correction 0.002 g

TABLE 14 (continued)

Net wt. of NH_3 vaporized . . . 1.381 g

- f. Wt. NH_3 x Heat of vaporization
per gram (Table 12) 1.381 g x 327 cal/g - 452
3. Heat of Reaction Measured - Heat of Vaporization
+ (Heat Capacity x ΔT) = 452 + (-139) 313
4. Heat of Reaction per Gram-atom Lithium Kcal
313 cal/0.00615 gram-atoms = ΔH_1 = -50.9

	Weight (g)	Specific Heat (cal/g $^{\circ}\text{C}$)	Heat Capacity (cal/ $^{\circ}\text{C}$)
1. NH_3	3.2423 g	0.81	0.1
2. Glass (Bulb, stirrer, etc.)	2.5	0.2	0.5
3. Lithium	0.0172	0.7	0.0
4. Platinum	8.4	0.03	0.3
5. Calorimeter (from fig. 10 for liquid height of 143.0 mm)			29.3
6. Sample in calorimeter:			
Weighed in	112.89		
Vaporized prior to reaction			
+ amount vaporized during reaction	0.37	1.088	119.7
Total for (4)	112.82		
Total Heat Capacity of system			141.0

C. Heat Effect

1. At a heat capacity of system = 0.361 x 141.0 - 50.9
2. Heat of vaporization
- Volume of gas-collecting system 5715 ml
 - Volume of H_2 evolved 0.002478
 - Vol. of H_2 evolved 501.2 mm, 25 $^{\circ}\text{C}$ 152.7 ml
 - Vol. of NH_3 evolved 501.2 mm, 25 $^{\circ}\text{C}$ 5452 ml
 - % of NH_3 vaporized 0.540% g
(no line pressure correction)
 - Wt. NH_3 x Heat of vaporization per gram (Table 12) 0.540% g x 327 cal/g - 175.7
3. Heat of Reaction Measured = - Heat of Vaporization + (Heat Capacity x ΔT) = -175.7 + 120.8
4. Heat of Reaction per Gram-atom Lithium
120.8 cal/0.002478 g ΔH_1 = - 48.8 Kcal

TABLE 15

SUMMARY OF CALCULATIONS FOR
EXPERIMENT E
(LITHIUM)

A. Temperature change

Average E (from temperature pattern)	1126.5 uv
Average T (Table 30)	-32.92 °C
dE/dT (Table 30)	-32.69 uv/°C
$\Delta E(\Delta T)$	11.8 uv
ΔT	-0.361 °C

B. Heat Capacity of System:

Item	Weight(g)	Specific Heat(cal/g/°C)	Heat Capacity(cal/°C)
1. NH ₄ Br	0.2429 g	0.21	0.1
2. Glass(Bulb, stirrer etc.)	2.5	0.2	0.5
3. Lithium	0.0172	0.7	0.0
4. Platinum	6.4	0.03	0.2
5. Calorimeter (From fig. 20 for liquid height of 142.0 mm.)			20.3
6. Ammonia in calorimeter:			
Weighed in	112.89		
Vaporized prior to reaction			
1/2 amount vaporized during reaction	0.27	1.065	119.9
Total for (6)	112.62		
Total Heat Capacity of System			141.0

C. Heat Effect

1. $\Delta T \times$ Heat capacity of system = -0.361 x 141.0 = -50.9
2. Heat of vaporization:
 - a. Volume of gas-collecting system 6715 ml
 - b. Moles of H₂ evolved 0.002478
 - c. Vol. of H₂ evolved @91.2mm, 25°C 252 ml
 - d. Vol. of NH₃ evolved @91.2mm, 25°C 6463 ml
 - e. Wt. of NH₃ vaporized 0.5406 g
(no line pressure correction)
 - f. Wt. NH₃ x Heat of vaporization per gram (Table 12) 0.5406 g x 327 cal/g = -176.7
3. Heat of Reaction Measured = - Heat of Vaporization + (Heat Capacity x ΔT) = -176.7 - 50.9 = -125.8
4. Heat of Reaction per Gram-atom Lithium
 $125.8 \text{ cal} / 0.002478 = \Delta H_1 = - 50.8 \text{ Kcal}$

STATE OF CALIFORNIA

DEPARTMENT OF
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1135.3
-02.32
-02.32
11.8
-0.381

Temperature change
Average (from temperature history)
Average (Table 20)
Average (Table 20)
Average (Table 20)
Average (Table 20)

Heat Capacity of System

Item	Weight (g)	Specific Heat (cal/g°C)	Heat (cal)
1. Water	1000	1.00	1000
2. Glass (bottle, stirrer, etc.)	100	0.2	20
3. Lithium	100	0.0175	1.75
4. Sodium	100	0.03	3
5. Calorimeter (from lit.)	100	0.03	3
6. Total liquid weight	100	0.03	3
7. Ammonia in calorimeter	100	0.03	3
8. Wet heat in	100	0.03	3
9. Vaporized	100	0.03	3
10. Heat of reaction	100	0.03	3
11. Total for (a)	100	0.03	3
12. Total heat capacity of system	100	0.03	3

113.5
1.005
0.27
Total for (a) 113.5
Total heat capacity of system 113.5

Heat Effect
1. At heat capacity of system 113.5 x 113.5 = 12866.25
2. Heat of vaporization
3. Volume of gas-collecting system 113.5 ml
4. Volume of H₂ evolved 0.002478
5. Volume of H₂ evolved 0.002478
6. Volume of H₂ evolved 0.002478
7. Volume of H₂ evolved 0.002478
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80. Volume of H₂ evolved 0.002478
81. Volume of H₂ evolved 0.002478
82. Volume of H₂ evolved 0.002478
83. Volume of H₂ evolved 0.002478
84. Volume of H₂ evolved 0.002478
85. Volume of H₂ evolved 0.002478
86. Volume of H₂ evolved 0.002478
87. Volume of H₂ evolved 0.002478
88. Volume of H₂ evolved 0.002478
89. Volume of H₂ evolved 0.002478
90. Volume of H₂ evolved 0.002478
91. Volume of H₂ evolved 0.002478
92. Volume of H₂ evolved 0.002478
93. Volume of H₂ evolved 0.002478
94. Volume of H₂ evolved 0.002478
95. Volume of H₂ evolved 0.002478
96. Volume of H₂ evolved 0.002478
97. Volume of H₂ evolved 0.002478
98. Volume of H₂ evolved 0.002478
99. Volume of H₂ evolved 0.002478
100. Volume of H₂ evolved 0.002478

TABLE 16

SUMMARY OF CALCULATIONS
EXPERIMENT F
(LITHIUM)

A. Temperature change			
Average E (from temperature pattern)		1143.5 uv	
Average T (from Table 30)		-33.44°C	
dE/dT (Table 30)		-32.63 uv/°C	
$\Delta E(\Delta \theta)$		18.3 uv	
ΔT		-0.561 °C	
B. Heat Capacity of System			
Item	Weight (g)	Specific Heat (cal/g/°C)	Heat Capacity (cal/°C)
1. NH ₄ Br	0.2429 g	0.21	0.1
2. Glass (Bulb stirrer, etc.)	2.5	0.2	0.5
3. Lithium	0.0172	0.7	0.0
4. Platinum	6.4	0.03	0.2
5. Calorimeter (From fig. 20 for liquid height of 140.9 mm)			20.0
6. Ammonia in calorimeter:			
Weighed in	113.21		
Vaporized prior to reaction			
½ amount vaporized during reaction	0.30	1.065	120.3
Total for (6)	112.91		141.1
Total Heat Capacity of System			141.1
C. Heat Effect			
1. $\Delta T \times$ Heat Capacity of System =	-0.561 x 141.1		-79
2. Heat of vaporization:			
a. Vol. of gas-collecting system	6715 ml		
b. Moles of H ₂ evolved	0.001198		
c. Vol. of H ₂ evolved @ 101.9mm, 25°C	219 ml		
d. Vol. of NH ₃ evolved @ 101.9mm, 25°C	6496 ml		
e. Wt. of NH ₃ vaporized (no line pressure correction)	0.6070 g		
f. Wt. NH ₃ x Heat of vaporization per gram (Table 12)	0.6070 x 327		-199
3. Heat of Reaction Measured = -Heat of Vaporization + (Heat Capacity x ΔT) =	199 - 79		120
4. Heat of Reaction per Gram-atom Lithium			
120 cal/0.002395 = ΔH_1 =	- 50.1 Kcal		

TABLE 1

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TABLE 17

SUMMARY OF CALCULATIONS
EXPERIMENT G
(LITHIUM)

A. Temperature change

Average E (from temperature pattern)	1136 uv
Average T (Table 30)	-33.20 °C
dE/dT (Table 30)	-32.65 uv/°C
$\Delta E(\Delta H')$	32.5 uv
ΔT	-0.995 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat (cal/g/°C)	Heat Capacity (cal/°C)
1. NH ₄ Br	0.5168	0.21	0.1
2. Glass (Bulb, Stirrer etc)	2.5	0.2	0.5
3. Lithium	0.0321	0.7	0.0
4. Platinum	6.4	0.03	0.2
5. Calorimeter (From fig. 20 for liquid height of 141.5 mm.)			20.2
6. Ammonia in calorimeter:			
Weighed in	112.97		
Vaporized prior to reaction			
1/2 amount vaporized during reaction	0.57	1.065	199.7
	112.40		
Total Heat Capacity of System			140.7

C. Heat Effect

1. $\Delta T \times$ Heat Capacity of system = -0.995 x 140.7 = -140
2. Heat of vaporization:
 - a. Vol. of gas-collecting system 6715 ml
 - b. Moles of H₂ evolved 0.00231
 - c. Vol. of H₂ evolved @190mm, 25°C 230 ml
 - d. Vol of NH₃ vaporized @190mm, 25°C 6485 ml
 - e. Wt. of NH₃ vaporized 1.132 g
 - line pressure correction 0.001 g
 - 1.133 g
 - f. Wt. of NH₃ x Heat of vaporization per gram (Table 12) 1.133g x 327cal/g = -371
3. Heat of Reaction Measured = - Heat of Vaporization + (Heat Capacity x ΔT) = 371 - 140 = 231
4. Heat of Reaction per Gram-atom Lithium
 $231 \text{ cal} / 0.00463 = \Delta H_1 = -50.0 \text{ Kcal}$

TABLE 18

SUMMARY OF CALCULATIONS

EXPERIMENT A

(CESIUM)

A. Temperature change

Average E (from temperature pattern)	1145.1 uv
Average T (Table 30)	-32.49°C
dE/dT (Table 30)	-32.63 uv/°C
$\Delta E(\Delta \theta')$	36.8 uv
ΔT	-1.13 C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat (cal/g/°C)	Heat Capacity (cal/°C)
1. NH ₄ Br	0.628	0.21	0.1
2. Glass (Bulb, stirrer etc.)	2.5	0.2	0.5
3. Cesium	0.7766	0.05	0.0
4. Platinum	6.4	0.03	0.2
5. Calorimeter (From fig. 20 for liquid Height of 139.9 mm.)			19.8
6. Ammonia in calorimeter:			
Weighed in	113.01		
Vaporized prior to reaction	1.35		
$\frac{1}{2}$ amount vaporized during reaction	0.61	1.065	118.0
	111.05		
Total Heat Capacity of System			138.6

C. Heat Effect

1. $\Delta T \times$ Heat Capacity of system = -1.13×138.6 -157
2. Heat of vaporization:
 - a. Vol. of gas-collecting system 6715 ml
 - b. Moles of H₂ evolved 0.002924
 - c. Vol. of H₂ evolved @ 205.2mm, 25°C 265 ml
 - d. Vol. of NH₃ evolved @ 205.2mm, 25°C 6450 ml
 - e. Wt. of NH₃ vaporized 1.214 g
 - line pressure correction 0.007 g
 - 1.221 g
 - f. Wt. of NH₃ x Heat of vaporization per gram (Table 12) $1.221g \times 327.3 \text{ cal/g} = 400$
3. Heat of Reaction Measured = -Heat of Vaporization + (Heat Capacity x ΔT) = $400 - 157$ 243
4. Heat of Reaction per Gram-atom Cesium
 $243 / 0.005848 = \Delta H_1 = -41.6 \text{ Kcal}$

TABLE 19
SUMMARY OF CALCULATIONS
EXPERIMENT C
(CESIUM)

A. Temperature change	
Average E (from temperature pattern)	1130.2 uv
Average T (Table 30)	-33.04°C
dE/dT (Table 30)	-32.68 uv/°C
$\Delta E(\Delta \theta')$	38.3 uv
ΔT	-1.17°C

B. Heat Capacity of System	Item	Weight (g)	Specific Heat (cal/g/°C)	Heat Capacity (cal/°C)
1.	NH ₄ Br	0.966	0.21	0.2
2.	Glass (Bulb, stirrer etc.)	2.5	0.2	0.5
3.	Cesium	1.1843	0.05	0.1
4.	Platinum	6.4	0.03	0.2
5.	Calorimeter (From fig. 20 for liquid height of 139.7 mm.)			119.8
6.	Ammonia in calorimeter:			
	Weighed in	113.14		
	Vaporized prior to reaction	0.10		
	½ amount vaporized during reaction	<u>0.81</u>	1.065	<u>119.5</u>
		112.23		
Total Heat Capacity of System				140.3

C.	Heat Effect		
1.	ΔT x Heat Capacity of system	= -1.17 x 140.3	-164
2.	Heat of vaporization:		
	a. Vol. of gas-collecting system	6715 ml	
	b. Moles of H ₂ evolved	0.004459	
	c. Vol. of H ₂ evolved @275.7mm, 25°C	301 ml	
	d. Vol. of NH ₃ evolved @275.7mm, 25°C	6414 ml	
	e. Wt. of NH ₃ vaporized	1.625 g	
	line pressure correction	<u>0.001 g</u>	
		1.626 g	
	f. Wt. of NH ₃ x Heat of vaporization per gram (Table 12) 1.626g x 326.9cal/g		-531
3.	Heat of Reaction Measured = - Heat of Vaporization + (Heat Capacity x ΔT)	= 531-164	367
4.	Heat of Reaction per Gram-atom Cesium		
	367 cal/0.008917 gram atoms = ΔH_1	= -41.2 Kcal	

TABLE 11 HEAT CAPACITY OF SYSTEM (CALORIES)

Temperature (°C)	Heat Capacity (cal/°C)
110.0	1.170
100.0	1.170
90.0	1.170
80.0	1.170
70.0	1.170
60.0	1.170
50.0	1.170
40.0	1.170
30.0	1.170
20.0	1.170
10.0	1.170
0.0	1.170

Item	Heat Capacity (cal/°C)	Weight (g)	Specific Heat (cal/g°C)
1. Nitrogen	0.985	0.51	0.2
2. Nitrogen, liquid	1.1845	0.5	0.2
3. Gasoline	0.4	0.05	0.2
4. Petroleum	0.4	0.05	0.2
5. Calorimeter (from 110.0 to 0.0)	118.8		
6. Ammonia in calorimeter	118.8		
7. Vaporized after reaction	0.10		
8. Vaporized during reaction	0.81	1.065	118.8
Total heat capacity of system	118.8		140.3

Item	Heat Capacity (cal/°C)	Weight (g)	Specific Heat (cal/g°C)
1. At x Heat Capacity of system = -1.17 x 140.3	-164		
2. Heat of vaporization:			
a. Vol. of gas-liquid system	0.004459	0.004459	0.2
b. Vol. of H ₂ evolved	0.001	0.001	0.2
c. Vol. of H ₂ evolved 22.5°C	0.001	0.001	0.2
d. Vol. of H ₂ evolved 22.5°C	0.001	0.001	0.2
e. Vol. of H ₂ vaporized	0.001	0.001	0.2
f. Heat of reaction measured = -164	1.635		
g. Heat of reaction per gram-atom Gasoline	1.635		
h. Heat of reaction per gram-atom = -41.3	1.635		

TABLE 20 SUMMARY OF CALCULATIONS
DETERMINATION OF THE HEAT OF SOLUTION OF
LITHIUM

A. Temperature change			
Average θ (from temperature pattern)			1106.3 uv
Average T (Table 30)			-32.30 °C
dE/dT (Table 30)			-32.74 uv/°C
$\Delta E(\Delta H')$			-2.9 uv
ΔT			0.089 °C
B. Heat Capacity of System			
Item	Weight (g)	Specific Heat (cal/g/°C)	Heat Capacity (cal/°C)
1. ---			
2. Glass, (Bulb, stirrer etc.)	2.5	0.2	0.5
3. Lithium	0.4977	0.7	0.4
4. Platinum	6.4	0.03	0.2
5. Calorimeter (From fig. 20 for liquid height of 144.9 mm.)			20.9
6. Ammonia in calorimeter:			
Weighed in	112.80		
Vaporized prior to reaction	1.07		
$\frac{1}{2}$ amount vaporized during reaction	1.03	1.064	117.8
	110.70		
Total heat Capacity of System			139.8
C. Heat Effect			
1. $\Delta T \times$ Heat Capacity of system =	0.089 x 139.8		12.4
2. Heat of vaporization:			
a. Vol. of gas-collecting system	6715 ml		
b. Moles of H_2 evolved			
c. Vol. of H_2 evolved			
d. Vol. of NH_3 evolved @ 334.5mm, 25°C	6715		
e. Wt. of NH_3 vaporized (no line pressure correction)	2.064 g		
f. Wt. NH_3 x Heat of vaporization per gram (Table 12)	2.064g x 326.4cal/g		-673.7
3. Heat of Reaction Measured = Heat of Vaporization + (Heat Capacity x ΔT)	= 673.7 12.4		686.1
4. Heat of Solution per Gram-atom Lithium	686.1 cal/0.0718 = ΔH_1		= -9550 cal

TABLE 21
SUMMARY OF CALCULATIONS
DETERMINATION OF THE HEAT OF SOLUTION OF
AMMONIUM BROMIDE

A. Temperature change

Average E (from temperature pattern)	1100.0 uv
Average T (Table 30)	-32.17 °C
dE/dT (Table 30)	-32.76 uv/°C
$\Delta E(\Delta H)$	-8.1 uv
ΔT	0.25 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat (cal/g/°C)	Heat Capacity (cal/°C)
1. NH ₄ Br	4.2909	0.21	0.9
2. Glass (Bulb, stirrer etc.)	4.1	0.2	0.8
3. ---			
4. ---			
5. Calorimeter (From fig. 20 for liquid height of 138.6 mm.)			19.5
6. Ammonia in calorimeter:			
Weighed in	111.17		
Vaporized prior to reaction	0.78		
½ amount vaporized during reaction	0.59	1.064	116.8
	109.80		
Total Heat Capacity of System			138.0

C. Heat Effect

1. $\Delta T \times$ Heat Capacity of system = 0.25×138.0 35
2. Heat of vaporization:
 - a. Vol. of gas-collecting system 6715 ml
 - b.
 - c.
 - d. Vol. of NH₃ evolved @190mm, 25°C 6715 ml
 - e. Wt. of NH₃ vaporized 1.172 g
 - (no line pressure correction)
 - f. Wt. NH₃ x Heat of vaporization per gram (Table 12) $1.172 \text{ g} \times 326 \text{ cal/g}$ -382
3. Heat of Reaction Measured = - Heat of Vaporization + (Heat Capacity x ΔT) = 382 35 417
4. Heat of Solution per mole of NH₄Br
 $417 \text{ cal} / 0.04379 \text{ moles} = \Delta H_1 = -9520 \text{ cal}$

TABLE 21 DETERMINATION OF THE HEAT OF VAPORIZATION OF ETHYL ALCOHOL

A. Temperature change

1100.0 W	1100.0 W
-32.19 °C	-32.19 °C
-52.78 W	-52.78 W
-5.1 W	-5.1 W
0.86 °C	0.86 °C

B. Heat capacity of system

Item	Weight (g)	Specific heat (cal/g °C)	Heat capacity (cal/°C)
1. Water	4.2009	0.91	0.8
2. Glass (Bulb, stirrer & etc.)	0.2	0.2	0.8
3. ...			
4. ...			
5. ...			
6. ...			
7. ...			
8. ...			
9. ...			
10. ...			
11. ...			
12. ...			
13. ...			
14. ...			
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95. ...			
96. ...			
97. ...			
98. ...			
99. ...			
100. ...			

C. Heat effect

1. At a heat capacity of system = 0.85 x 128.0	35
2. Heat of vaporization:	
a. Vol. of gas-collecting system	6715 ml
b. ...	
c. ...	
d. Vol. of gas evolved (100 mm, 25°C)	6715 ml
e. Vol. of gas vaporized	1.172 g
f. (no line pressure correction)	
g. Heat of vaporization per gram (1.172 g x 326 cal/g)	-382
h. Heat of reaction measured = heat of vaporization (Heat Capacity x ΔT) = 382.35	417
i. Heat of solution per mole of H ₂ O	
j. 417 cal / 0.04375 moles = 9520 cal	

TABLE 22

SUMMARY OF THE EXPERIMENTS

Experiment	Sample size grams	Moles $\text{NH}_3/\text{g-}$ atom alkali metal	ΔH (Kcal) 1	ΔH_1 (Kcal) (corrected) ^x
C (Lithium)	0.0426	1060	-50.9	-51.1
E. (Lithium)	0.0172	2670	-50.8	-51.0
F (Lithium)	0.0166	2770	-50.1	-50.3
G (Lithium)	0.0321	1430	<u>-50.0</u>	<u>-50.2</u>
		Mean	-50.5	-50.7
A (Cesium)	0.7766	1140	-41.6	
C (Cesium)	1.1843	745	<u>-41.2</u>	
		Mean	-41.4	

Heat of Solution of Lithium	Sample size (gram)	Moles $\text{NH}_3/\text{g-}$ atom Li	ΔH_2 (cal)	ΔH_2 (cal) (corr) ^x
	0.4977	90.6	-9,550	-9,610

Heat of Solution of Ammonium Bromide	Sample size (grams)	Moles $\text{NH}_3/\text{g-}$ moles NH_4Br	$\Delta H_{\text{Solution}}$ (calories)
	4.2909	147	-9,520

^x Corrected values obtained from considerations of the reported impurities in the samples of lithium used, as discussed on page 56.

TABLE 22

ANALYSIS OF THE EXPERIMENT

Experiment Sample size from alkali metal	ΔH (cal) f	ΔH (cal) x (corrected)
C (Lithium) 0.0436	1080	-50.9
E (Lithium) 0.0172	2870	-50.8
F (Lithium) 0.0165	2770	-50.1
G (Lithium) 0.0321	1430	-50.0
Mean		-50.7
A (Cesium) 0.7788	1140	-41.8
C (Cesium) 1.1842	745	-41.2
Mean		-41.4

Heat of solution Sample size
from Li (corrected) ΔH₂ (cal) ΔH₂ (cal) ΔH₂ (cal)

0.4977 90.6 -9.580 -9.810

H

Sample size Moles NH₃ ΔH₂ (cal) ΔH₂ (cal) ΔH₂ (cal)

1.2909 147 -9.580

* Corrected values obtained from consideration of the reported impurities in the samples of lithium used, as discussed on page 22.

TABLE 23

THE HEAT OF REACTION ΔH_3 FROM THE
EXPERIMENTAL RESULTS

Experiment	Alkali Metal	Ammonium Salt	Moles NH_3 gram-atom metal	ΔH_1 Kcal	ΔH_2 Kcal	ΔH_3 Kcal
This research						
C	Li	NH_4Br	1060	-51.1	-8.0 (Ref. 12) ^b	-43.1
E	Li	NH_4Br	2670	51.0	8.0	43.0
F	Li	NH_4Br	2770	50.3	8.0	42.3
G	Li	NH_4Br	1430	50.2	8.0	42.2
Ref. 10	Li	NH_4Br		-49.5	-8.0	-41.5
Ref. 10	Li	NH_4Br		50.3	8.0	41.3
MEAN	Li	NH_4Br		-50.5	-8.0 (9.6) ^x	-42.5 (-40.9) ^x
Ref. 10	Na	NH_4Cl		-38.8	1.4 (Ref. 11)	-40.2
Ref. 10	Na	NH_4Cl		39.0	1.4	40.4
Ref. 10	Na	NH_4Cl		39.2	1.4	40.6
Ref. 10	Na	NH_4Cl		39.1	1.4	40.5
Ref. 10	Na	NH_4Cl		38.6	1.4	40.0
Ref. 10	Na	NH_4Br		38.3	1.4	39.7
Ref. 10	Na	NH_4Br		38.4	1.4	39.8
MEAN	Na			-38.7	1.4	-40.1
Ref. 10	K	NH_4Br		-39.9	0.0 (Ref. 12) ^b	-39.9
Ref. 10	K	NH_4Br		39.5	0.0	39.5
Ref. 10	K	NH_4Br		39.6	0.0	39.6
MEAN	K			-39.7	0.0	-39.7
This research						
A	Cs	NH_4Br	1140	-41.6	0.0 (Ref. 12) ^b	-41.6
C	Cs	NH_4Br	745	41.2	0.0	41.2
MEAN	Cs			-41.4	0.0	-41.4

^x Value of ΔH_2 obtained in this research

^{xx} Value of ΔH_3 based upon the value of ΔH_2 which was obtained in this research.

The heats of reaction of lithium and cesium metals with the ammonium ion measured in this research are presented in Table 2. The values of ΔH_1 , the heat of the reaction of the solvated electron with the ammonium ion, are obtained upon combining of values of ΔH_1 for the reaction of the solid metal with the ammonium ion, and corresponding values of ΔH_2 . Literature values of the heats of solution of the respective alkali metals in pure liquid ammonia. Table 2 represents a summary of these values of ΔH_1 and ΔH_2 to give ΔH_3 values. Included in Table 2 are values of ΔH_1 for cesium metal, cesium metal and two values for lithium metal which were determined in a previous unpublished research by G. L. Kuznetsov. The agreement among the values of ΔH_3 in Table 2 (the maximum deviation from the mean being about 2%), indicates that there is a common species, which may be the solvated electron, present in the alkali solutions of all the alkali metals, i.e., that the value of ΔH_3 is independent of the alkali metal used in the reaction. It seems to be a difference in the value of ΔH_1 is a very small difference, amounting to only a fraction of a percent from the experimental error of 2% in the most discordant example, that of cesium metal. This small difference can be explained away by pointing to the fact that certain of the calculations made regarding the solutions fail in this case.

It might be well to point out the fact that in the calculations of ΔH_2 for these experiments there are two places where a small error is greatly magnified. The first of these occurs in obtaining ΔT or rather $\Delta \theta'$, a relatively small value as the difference between two large values. The other is in evaluating the molar heat of reaction by dividing the net heat effect, values averaging about 250 calories, by the number of gram ions of alkali metal reacting, averaging the order of magnitude of 1×10^{-2} . The result is a magnification of any small error occurring in the value for the net heat effect.

In calculating ΔH_3 for these reactions certain assumptions regarding the solutions used have been made. For example, complete dissociation of the electrolytes is assumed. This is a reasonable assumption since the concentration of these solutions averaged between 0.15 and 0.015 molar. Also it has been assumed that the relative heat content of the ammonium bromide or chloride in the dilute solution were not appreciably different from that of the resulting alkali metal bromide or chloride after the reaction had taken place. This assumption was sustained by experiment using a wide range of sample sizes of lithium and ammonium bromide. With a six-fold change in lithium sample size no trend in the value of the heat of reaction was observed.

The heats of solution tabulated as ΔH_2 in table 23 have been taken from the literature as indicated. Upon combination of the literature value of ΔH_2 for lithium with the measured

It might be well to point out the fact that in the calculations of ΔH_f for these experiments there are two places where a small error is readily manifested. The first of these occurs in obtaining ΔT or rather $\Delta\theta$, a relatively small value as the difference between two large values. The other is in evaluating the molar heat of reaction by dividing the net heat effect values averaging about 250 calories by the number of gram ions of alkali metal reacting averaging the order of magnitude of 1×10^{-2} . The result is a magnification of any small error occurring in the value for the net heat effect.

In calculating ΔH_f for these reactions certain assumptions regarding the solutions used have been made. For example, complete dissociation of the electrolytes is assumed. This is a reasonable assumption since the concentration of these solutions averaged between 0.15 and 0.015 molar. Also it has been assumed that the relative heat content of the ammonium bromide or chloride in the dilute solution were not appreciably different from that of the resulting alkali metal bromide or chloride after the reaction had taken place. This assumption was substantiated by experiment during a wide range of sample sizes of lithium and ammonium bromide. With a six-fold change in lithium sample size no trend in the value of the heat of reaction was observed.

The heats of solution tabulated as ΔH_s in table 23 have been taken from the literature as indicated. Upon comparison of the literature value of ΔH_s for lithium with the reported

MOLAR HEAT OF SOLUTION
CALORIES

10,000

9,000

8,000

50

100

150

200

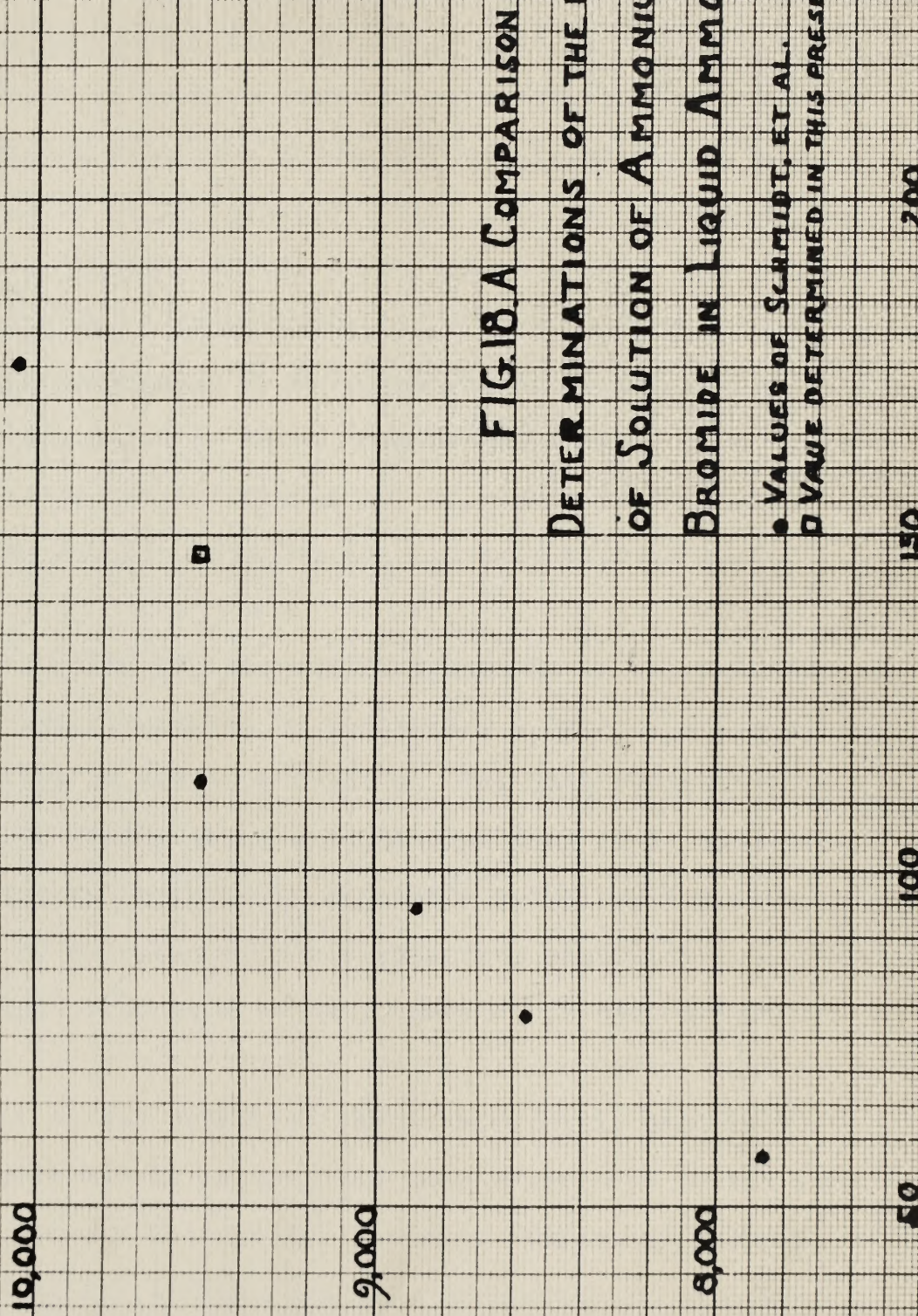
MOLES OF NH_3 PER MOLE NH_4Br

FIG. 18. A COMPARISON OF

DETERMINATIONS OF THE HEAT
OF SOLUTION OF AMMONIUM
BROMIDE IN LIQUID AMMONIA.

• VALUES OF SCHMIDT, ET AL.

□ VALUE DETERMINED IN THIS PRESENT WORK



values of ΔH_1 for lithium, a value of ΔH_3 that was noticeably out of line with the values of ΔH_3 calculated for the other alkali metals occurred. The heat of solution of lithium was shown by Schmidt to be a function of concentration and to approach a limiting value for moderately dilute solutions which was considered to be the value for the infinitely dilute solution. However, because of the above discrepancy in the value of ΔH_3 for lithium, a redetermination of the heat of solution of lithium was undertaken at a concentration corresponding to the more dilute region in which Schmidt had worked. The value 9.6 Kcal obtained was definitely out of line with the value 8.0 Kcal which Schmidt reported for the heat of solution of lithium.

The possibility of inherent disagreement in the methods or apparatus was discounted by conducting a determination of the heat of solution of ammonium bromide. The data summarized in figure 18 shows that a value was obtained that is in agreement within experimental error with Schmidt's value for ammonium bromide heat of solution at a corresponding concentration, if an experimental error of 1 to 2% is assumed in each determination.

No report on the purity of the lithium metal used by Schmidt was made and it is probable that impurities in the samples used by him may account for the wide difference between his value of ΔH_2 for lithium and that determined in this research.

values of ΔH for lithium, a value of ΔH that was noticeably
out of line with the values of ΔH calculated for the other
alkali metals occurred. The heat of solution of lithium was
shown by Schmidt to be a function of concentration and to ap-
proach a limiting value for moderately dilute solutions which
was considered to be the value for the infinitely dilute solu-
tion. However, because of the above discrepancy in the value
of ΔH for lithium, a re-determination of the heat of solution
of lithium was undertaken at a concentration corresponding to
the more dilute region in which Schmidt had worked. The value
of 2.8 Kcal obtained was definitely out of line with the value
of 5.5 Kcal which Schmidt reported for the heat of solution of
lithium.

The possibility of inherent disagreement in the methods
or apparatus was discounted by conducting a determination of the
heat of solution of ammonium bromide. The data summarized in
Figure 18 shows that a value was obtained that is in agreement
with experimental error with Schmidt's value for ammonium
bromide heat of solution at a corresponding concentration. It
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No report on the purity of the lithium metal used by
Schmidt was made and it is probable that impurities in the sam-
ples used by him may account for the wide difference between
the value of ΔH for lithium and that determined in this re-
search.

The somewhat high value of ΔH_3 in the case of cesium metal solutions could be attributed to the presence of a small amount of sodium as an impurity in the cesium. Thus, if 0.5% by weight of sodium were present, one g-atom of sample weighed on the basis of pure cesium actually would supply 1.026 g-atoms of solvated electrons producing a measured heat of reaction 2.6% too large.

Sample - 133 g (assumed to be pure Cs.)

	G-atoms assumed	Actual g-atoms
Sample - 133 g	1	
133 g x 0.995 = 132.3 g Cs		0.996
133 g x 0.005 = 0.03 g Na		<u>0.03</u>
Gram-atoms of solvated electrons	1	1.026

The heats of reaction of lithium and cesium with the ammonium ion have been measured. Procedures for preparing samples and improvements in the apparatus for making calorimetric measurements are described.

Agreement of $\pm 2\%$ amongst the values for ΔH_3 for lithium, sodium, potassium and cesium solutions is interpreted as evidence for the presence of a common species considered to be the solvated electron in the dilute solutions of the alkali metals. Any differences that might exist from an energy point of view appear to be quite small.

The somewhat high value of ΔH_f° in the case of cesium metal
 adjustments could be attributed to the presence of a small amount
 of sodium as an impurity in the cesium. Thus, if 0.5% by weight
 of sodium were present, one gram of sample yielded on the
 basis of pure cesium actually would supply 1.032 g-atoms of
 univalent electrons producing a measured heat of reaction 8.52
 cal. later.

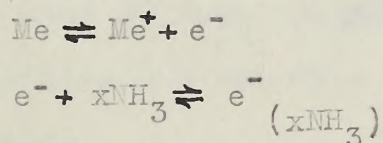
Sample - 1.3 g (assumed to be pure Cs.)

G-atoms assumed	Actual g-atoms
Sample - 1.3 g	1
$1.3 \text{ g} \times 0.995 = 1.2935 \text{ g Cs}$	
$1.3 \text{ g} \times 0.005 = 0.0065 \text{ g Na}$	
G-atoms of univalent electrons	
1.032	1

The heat of reaction of lithium and cesium with the ammon-
 ium ion have been measured. Procedures for preparing samples
 and measurements in the apparatus for making calorimetric
 measurements are described.
 Agreement of $\pm 2\%$ amongst the values for ΔH_f° for lithium,
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 vated electron in the dilute solutions of the alkali metals.
 Any differences that might exist from an energy point of view
 appear to be quite small.

VI ABSTRACT

The blue dilute solutions that are formed when small quantities of the alkali metals are dissolved in anhydrous liquid ammonia have been the object of much study, at first qualitatively but later more quantitatively. The unusual properties of these solutions were carefully studied by Kraus in particular who, on the basis of conductivity studies, regarded the dilute solutions of all the alkali metals as containing a common negative ion, the solvated electron, which he felt was responsible for all the observed properties. The following equilibria in all the solutions were postulated by Kraus:



Additional evidence of the presence in all the dilute solutions of a common species, possibly the solvated electron, was to be found in absorption spectrum studies. Absorption by solutions of all the alkali metals was found identical. Also, magnetic studies and photoelectric measurements pointed to the presence of the solvated electron in dilute solutions of the alkali metals. While the actual structure to be associated with the dilute solutions has not been determined the presence of a common species is strongly suggested by all these foregoing studies.

Similarities in various properties of the dilute solutions have thus been associated with the presence in each of a common

VI ABSTRACT

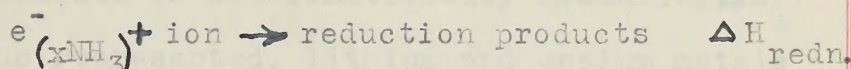
The dilute solutions of the alkali metals in various solvents have been the subject of much study, at least qualitatively. The general properties of these solutions were carefully studied by Evans in 1912, who, on the basis of conductivity studies, regarded the dilute solutions of all the alkali metals as containing a common negative ion, the solvated electron, which he felt was responsible for all the observed properties. The following equilibria in all the solutions were postulated by Evans:



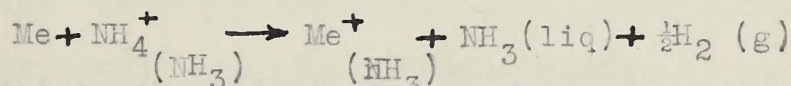
Additional evidence of the presence in all the dilute solutions of a common species, possibly the solvated electron, was to be found in absorption spectrum studies. Absorption by solutions of all the alkali metals was found identical. Also, magnetic studies and photoelectric measurements pointed to the presence of the solvated electron in dilute solutions of the alkali metals. While the actual structure to be associated with the solvated electron has not been determined the presence of a common species is suggested by all these facts.

Similarities in various properties of the dilute solutions have also been associated with the presence in each of a common

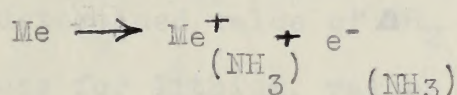
species. For present purposes it has been felt that if some such property as a heat of reduction of an ion by the solvated electron could be shown to have the same value for all the alkali metal solutions the presence of the solvated electron considered as a species common to all the solutions could be confirmed:



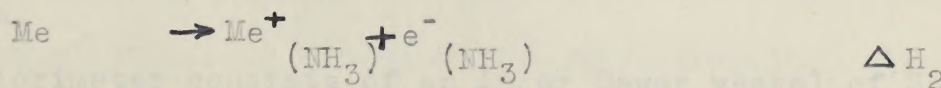
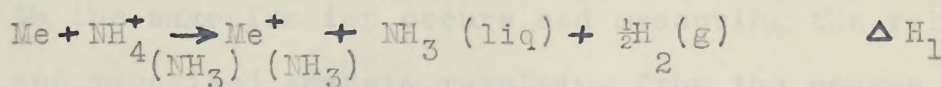
Direct determination of this heat of reduction is not feasible, so recourse to an indirect method of obtaining the reaction heat was rewarded with success. The reaction:



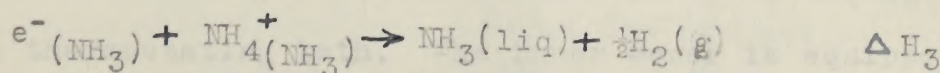
which represents the reaction of a solid alkali metal with the ammonium ion with a heat of reaction ΔH_1 may be combined with the reaction representing the solution of the solid alkali metal in pure liquid ammonia;



which has a heat effect ΔH_2 , to give a reaction which represents the ammonium ion being reduced by the solvated electron and which has a heat of reaction ΔH_3 :



subtracting and rearranging,



$$(\Delta H_3 = \Delta H_1 - \Delta H_2)$$

The heat of reduction ΔH_3 should be independent of the alkali metal used if all their solutions have in common some species as the solvated electron.

This research consists of calorimetrically measuring ΔH_1 for the first reaction represented, lithium and cesium metals reacting with the ammonium ion in liquid ammonia.

These ΔH_1 values have then been combined with corresponding ΔH_2 values from the literature to obtain calculated values for ΔH_3 .

Incidental to the principal procedures, a redetermination of the heat of solution, ΔH_2 , for lithium metal was undertaken, and the value obtained, not in accord with the literature value, has been shown to be more reasonable on the basis of purity of sample. This redetermined value of ΔH_2 gave, when combined with measured ΔH_1 values for lithium, values of ΔH_3 more in line with the general findings.

The calorimetric determination of ΔH_1 involves measuring the temperature change of the system in which the reaction of the metal with the ammonium ion occurs and measuring the volume of hydrogen and vaporized ammonia resulting from the course of the reaction.

The calorimeter consists of an inner Dewar vessel of 2 00 ml. capacity surrounded by an outer Dewar containing liquid ammonia as a thermostating bath. The inner Dewar is equipped with a solenoid actuated stirrer, a thermocouple, and a rod to

which is attached a fragile bulb containing the alkali metal sample. The respective alkali metal samples in the fragile bulbs are caused to react with the ammonium ion (present in the liquid ammonia from dissolved ammonium salt) in the calorimeter upon crushing of the sample-bulb. The temperature of the calorimeter and contents is followed at one minute intervals by means of the thermocouple. The gases evolved are led through a line into a thermostated vessel of measured volume where the resulting pressure of the collected gases is indicated by an attached manometer. The liquid height in the calorimeter, completely silvered save for a narrow vertical band to allow observation of the contents, is measured with a cathetometer.

Successive measurements according to the above procedure have been made with a variety of sizes of lithium samples and of cesium samples. The data has been tabulated as values of ΔH_1 . The mean value of ΔH_1 for lithium is -50.5 Kcal, for cesium -41.4 Kcal. Detailed reproductions of the actual data obtained in the laboratory have been included.

Calculations of ΔH_1 for a particular experiment from the recorded data has been described in detail for one experiment and summarized for each of the others.

The temperature pattern of the calorimeter is first plotted after thermocouple readings are converted to microvolts. Treatment of the temperature pattern by means of the Regnault-Pfaundler equation that takes into account the characteristics of the calorimeter yields the temperature change that has accompanied the reaction. This ΔT in microvolts is changed to

which is equipped with a thermistor and contains the alkali metal
 sample. The respective alkali metal samples in the thermistor
 are coupled to react with the ammonium ion present in the liquid
 medium. From dissolved ammonium salt in the calorimeter upon
 formation of the sample. The temperature of the calorimeter
 and reaction is followed at the minute intervals by means of the
 thermocouple. The gases evolved are led through a line into a
 faceted vessel of measured volume where the reacting gas-
 rate of the collected gases is indicated by an attached manometer.
 The liquid height in the calorimeter, completely silvered save
 for a narrow vertical band to allow observation of the contents,
 is measured with a cathetometer.

Successive measurements according to the above procedure
 have been made with a variety of sizes of lithium samples and at
 various rates. The data has been tabulated as values of ΔH .
 The mean value of ΔH for lithium is $-80.3 \text{ kcal. per gram}$
 $-11.4 \text{ kcal. per mole}$. Detailed reductions of the actual data obtained
 in the laboratory have been included.

Calculations of ΔH for a constant-volume experiment from the re-
 corded data has been described in detail for one experiment and
 are applied for each of the others.

The temperature pattern of the calorimeter is first plotted
 after thermocouple readings are converted to microvolts. Great-
 est of the temperature pattern by means of the logarithmic
 transfer of a line that takes into account the characteristics
 of the calorimeter yields the temperature change that has
 accompanied the reaction. This ΔT in microvolts is changed to

ΔT in degrees centigrade by use of values of dE/dT obtained in the calibration of the thermocouple.

The total heat capacity of the calorimeter and all components therein, obtained as a summation of the individual heat capacities, when multiplied by the ΔT calculated as above yields the quantity of heat producing the observed ΔT .

The quantity of heat extracted from the calorimeter by the vaporization of some of the solvent, liquid ammonia, during the reaction, is evaluated from the observed pressure of the collected gases and the known volume of the collecting vessel. The volume of hydrogen evolved, calculated by assuming the perfect gas law, considering one-half mole of hydrogen to be evolved for each gram-atom of alkali metal reacting, is subtracted from the total volume of the vessel to show the volume of the ammonia vapor. The weight of ammonia vapor is then calculated by use of Berthelot's equation of state. Multiplication of this weight of ammonia by the value of the heat of vaporization per gram of ammonia gives the quantity of heat extracted.

The quantity of heat evolved by the reaction of the given sample of alkali metal with the ammonium ion is now calculated by adding together, with respect to sign, the quantity of heat producing the observed ΔT and the quantity of heat extracted by the vaporized ammonia. This latter quantity is given a negative sign to indicate heat being extracted from the system. The resulting quantity of heat is then divided by the number of gram-atoms of alkali metal reacting to find the heat of reaction,

ΔT is the temperature of the water of value of ΔT obtained in the reaction of the substance.

The total heat capacity of the calorimeter and all contents is determined, obtained as a summation of the individual heat capacities, and multiplied by the ΔT indicated as above yields the quantity of heat evolved in the reaction ΔH .

The quantity of heat extracted from the calorimeter by the vaporization of some of the liquid, in this amount, during the reaction, is evaluated from the observed pressure of the collected gases and the known volume of the collecting vessel. The volume of hydrogen evolved, calculated by assuming the density of hydrogen, consisting of one-half mole of hydrogen to be evolved for each gram-atom of alkali metal reacting, is subtracted from the total volume of the vessel to show the volume of the ammonia vapor. The weight of ammonia vapor is then calculated by the density of ammonia vapor. Multiplication of this weight of ammonia by the value of the heat of vaporization per gram of ammonia gives the quantity of heat extracted.

The quantity of heat evolved by the reaction of the given sample of alkali metal with the ammonia can be now calculated by adding together, with respect to sign, the quantity of heat evolved in the observed ΔT and the quantity of heat extracted by the vaporized ammonia. This latter quantity is given a negative sign in the case heat being extracted from the system. The resulting quantity of heat is then divided by the number of gram-atoms of alkali metal reacting to find the heat of reaction.

ΔH_1 , per gram atom.

The values of ΔH_1 have been combined with corresponding values of ΔH_2 from the literature to give ΔH_3 values in a large summarizing table. For lithium, $\Delta H_1 = -50.5$ Kcal, ΔH_2 , the value obtained in this research, = 9.6 Kcal. Thus $\Delta H_3 = -40.9$ Kcal. For cesium, $\Delta H_1 = -41.4$, $\Delta H_2 = 0.0$, and $\Delta H_3 = -41.4$ Kcal. Included in the summarizing table are values obtained in a former unpublished research by Coulter of ΔH_1 for sodium and potassium metals. These, when combined with the respective ΔH_2 values yield ΔH_3 for sodium = -40.1 Kcal, for potassium, -39.7 Kcal.

Agreement of $\pm 2\%$ amongst these values for ΔH_3 for all the alkali metals indicates the presence in the dilute solutions of a common species which may be the solvated electron. Any difference in the value of ΔH_3 from metal to metal has been shown not to be significantly greater than the experimental error.

ΔH_f per gram atom.

The values of ΔH_f have been compared with corresponding values of ΔH_f from the literature to give ΔH_f values in a table summarizing table. For lithium, $\Delta H_f = -30.5$ kcal, ΔH_f the value obtained in this research, $\Delta H_f = -30.5$ kcal, $\Delta H_f = -30.5$ kcal. For cesium, $\Delta H_f = -41.4$, $\Delta H_f = 0.0$, and $\Delta H_f = -41.4$ kcal. Indicated in the summarizing table are values obtained in a table summarized research by Goulet of ΔH_f for sodium and potassium metals. These, when combined with the respective ΔH_f values yield ΔH_f for sodium = -40.1 kcal, for potassium, -39.7 kcal.

Agreement of $\pm 2\%$ amongst these values for ΔH_f for all the alkali metals indicates the presence in the dilute solutions of a common species which may be the solvated electron. Any difference in the value of ΔH_f from metal to metal has been shown not to be significantly greater than the experimental error.

VII Appendix

A. Calibration of the Copper Constantan Thermocouple

With one of its junctions maintained at a constant temperature such as is afforded by an ice-water mixture while the other junction is heated through a range of temperatures, a thermocouple will produce an E.M.F. the plot of which against temperatures of the heated junction is a parabola for most metals. For relatively small temperature differences and at a lower temperatures, however, the relationship between E.M.F. and temperature approaches linearity.

A thermocouple to be used in a limited range of temperatures is calibrated by observing the E.M.F. of the couple at two fixed points. The information thus gained is utilized in constructing an equation relating E.M.F. and temperature.

For this research, thermocouple TC-1 was calibrated at the sublimation point of solid CO_2 and at the melting point of mercury.

1. Experimental

The procedure for determining the E.M.F. developed by the thermocouple at the sublimation point of CO_2 is a straightforward one. In a small Dewar flask, a coil of manganin wire of 100 ohms resistance is buried beneath a large quantity of finely powdered dry ice. The leads of the coil are connected to a source of suitable current, several amperes and several volts. The thermocouple junction is imbedded in the dry ice while the reference junction is placed in a small Dewar with pure, crushed

05850

DECEMBER

EFFICIENCY BOND

THE STATE OF TEXAS, COUNTY OF DALLAS, do hereby certify that the within and foregoing is a true and correct copy of the original as the same appears in the records of the County Clerk of said County.

Witness my hand and the seal of said County at Dallas, Texas, this 1st day of December, 1905.

County Clerk of Dallas County, Texas.

1. Examined and found correct.

2. Attest my hand and the seal of said County at Dallas, Texas, this 1st day of December, 1905.

County Clerk of Dallas County, Texas.

3. Attest my hand and the seal of said County at Dallas, Texas, this 1st day of December, 1905.

County Clerk of Dallas County, Texas.

ice. After balancing of the potentiometer circuits, the E.M.F. of the thermocouple is observed at five minute intervals. The potentiometer is adjusted each time to read the exact value of the E.M.F. set up in the couple. A current of 0.1 ampere produces heat in the buried coil sufficient to maintain a slow stream of gaseous CO_2 sweeping out of the Dewar. Increase from 0.1 ampere to 1 ampere input of the heater produced no measurable change in the final equilibrium temperature attained by the subliming CO_2 . It is necessary to continue observations of the E.M.F. of the couple until such a steady value is reached. The barometric pressure is observed several times during the course of the measurement. Arrangement of the data is shown in Table 24.

By the same general procedure cooling and melting curves of triply distilled mercury were employed to calibrate the thermocouple at -38.87°C . The data is presented in Table 25.

2. Calculations

The sublimation temperature of solid CO_2 is calculated from the barometric pressure by substituting into equation (9):

$$\log p = 9.81137 - \frac{1349}{t^\circ \text{C} + 273.16} \quad (9)$$

Where p = barometric pressure in mm. and t = temperature in degrees centigrade at which sublimation of CO_2 occurs. The observed pressure is corrected for temperature effects:

18. Temperature: Its Measurement and Control, American Institute of Physics, Reinhold Publishing Co., N.Y.

19. Livingstone, Physico-Chemical Experiments, Macmillan Company, N.Y.

After a careful study of the data obtained from the
experiments it was found that the rate of reaction
is proportional to the concentration of the reactants
and is independent of the concentration of the products.
The rate of reaction is also independent of the concentration
of the catalyst.

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TABLE 24

EXPERIMENTAL DATA

DATE April 21, 1947
 Thermocouple Calibration
 Data Using Solid
 Carbon Dioxide

E.M.F. Measurements

Time (minutes)	Potentio- meter setting (uv)	Scale Readings		Sensi- tivity Scale div. per uv	Notes
		R ₀	R		
1					Heating cur- rent equals 0.2 amp.
7	2515	27.8	27.1		
	2520	27.8	34.0	1.38	
13	2515	27.8	27.0		
13½	2520	27.8	33.8	1.36	Heating cur- rent increas- ed to 0.3amp.
25	2515	27.7	26.8		
	2520	27.7	33.7	1.38	
					Heating cur- rent reduced to 0.1 amp.
					Atmospheric pressure: 773.20 mm.
					T = 25.45°C at barometer
37	2515	27.7	27.2		
	2520	27.8	34.2	1.40	

DATE April 21, 1957
 Location: Carbon Dioxide
 Station: Carbon Dioxide

EXPERIMENTAL DATA

TABLE 1

1.1.1. Measurements

Time (minutes)	Potential (mv)	Scale Reading R ₀	Scale Reading R	Barometric Pressure (mm Hg)	Notes
1					Heating coil - vent opened 0.5 amp.
2	2315	27.8	27.1		
	2320	27.8	24.0	1.35	
13	2315	27.8	27.0		Heating coil - vent increased to 0.5 amp.
14	2320	27.8	23.5	1.35	
25	2315	27.7	23.3		
	2320	27.7	23.7	1.35	
26	2315	27.7	27.8		Heating coil - vent reduced to 0.1 amp.
	2320	27.8	24.2	1.40	

Atmospheric
 pressure:
 775.30 mm.

T = 23.45°C

at pressure

TABLE 25

SUMMARY OF CALCULATIONS FOR
THERMOCOUPLE CALIBRATION USING SOLID
CARBON DIOXIDE AND MERCURY

Observed pressure 773.2 mm @ 25.45°C
Corrected pressure 770.0 mm

Calculated Boiling point
of solid CO₂ using equation 9 -78.37°C

E.M.F. of Thermocouple TC-1
at -78.37°C 2515.9 uv

Transition point of mercury - 38.87°C

E.M.F. of thermocouple TC-1
at -38.87°C 1319.1 uv

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 UNIVERSITY OF CALIFORNIA LIBRARY
 CARSON LIBRARY AND MUSEUM

Table 23

Observed pressure 773.2 mm @ 25.45°C
 Corrected pressure 770.0 mm

Calculated boiling point
 of solid CO₂ using equation 2 -78.27°C

E.M.F. of thermocouple TC-1
 at -78.27°C 2512.9 mv

Transition point of mercury - 38.87°C

E.M.F. of thermocouple TC-1
 at -38.87°C 1312.7 mv

$$p = \frac{1 + 1.84 \times 10^{-5} \times t^{\circ\text{C}}}{1 + 1.818 \times 10^{-4} \times t^{\circ\text{C}}} + P_{\text{obs}} \quad (10)$$

Where p = corrected pressure, P_{obs} = observed pressure and t = temperature in $^{\circ}\text{C}$ at the barometer.

A calibration table for the thermocouple is set up by use of the collected data. Three available methods for establishing such a table may be utilized. Of the three one method is considered preferable in that it yields values in a range intermediate to those given by the other two.

The first method used is that presented by Wiehe and Brevoort.²⁰ Equation (11) expresses the relationship between temperature and E.M.F. of their standard thermocouple:

$$E_{\text{st}} = 92.20 t - 29770 (1 - e^{-0.0018 t}) \quad (11)$$

where E_{st} = E.M.F. in uv of the standard thermocouple and t = corresponding temperature in $^{\circ}\text{C}$.

Equation (11) gives E.M.F. values E_{st} , CO_2 and $E_{\text{st}}(\text{Hg})$ when the corresponding temperatures T_{CO_2} and T_{Hg} are substituted for t .

Deviations between E.M.F. values thus calculated and the respective values actually observed with thermocouple TC-1 are used in evaluating the constants a and b in equation (12).

$$\text{Deviation} = aE_{\text{st}}^2 + bE_{\text{st}} \quad (12)$$

Solving equation (11) for values of E_{st} at T_{Hg} and T_{CO_2}

T	E_{st}
$(T_{\text{Hg}}) - 38.87^{\circ}\text{C}$	1426.4 uv
$(T_{\text{CO}_2}) - 78.37$	2715.5

$$y = \frac{141.54 \times 10^{-5} + 0.0001}{141.54 \times 10^{-5} + 0.0001}$$

where y is corrected pressure, P_c , at observed pressure and T is temperature in °C at the separator.

A relation for the thermodynamic is not by use of the collected data. Three available methods for calculating P_c and T_c may be utilized. Of the three one is chosen to be utilized in this report in that it yields values in a range consistent with those given by the other two.

The third method used is that presented by Viana and MacLeod. Equation (11) expresses the relationship between the

critical and R.M.P. of each standard thermodynamic:

$$R_c = 12.20 + 0.001 (1 - 0.001 T_c) \quad (11)$$

where R_c is R.M.P. in lb of the standard thermodynamic and T_c is critical temperature in °C.

Equation (11) gives R.M.P. values R_c and T_c when the corresponding temperatures T_{CO_2} and T_c are substituted for

Deviations between R.M.P. values R_c are calculated and the corresponding values observed with thermodynamic 10-1 are used in evaluating the constant k in equation (12).

$$k = \frac{R_c - 12.20}{T_c - 0.001 T_c} \quad (12)$$

Equation (12) for values of T_c at the T_{CO_2}

at

$$(13) \quad - 32.370$$

$$(14) \quad - 78.37$$

Next, the deviations are calculated; $E_{TC-1} - E_{st} = \text{Deviation}$

E_{st}	$E_{(TC-1)}$	Deviation ($E_{obs} - E_{st}$)
1426.4 uv	1319.1 uv	-107.3 uv
2715.5	2515.9	-199.6

Inserting the respective values in equation (12),

$$-107.3 = a \cdot 1426.4 + b(1426.4)^2$$

$$-199.6 = a \cdot 2715.5 + b(2715.5)^2$$

Solving these simultaneously;

$$a = -0.07712$$

$$b = 1.334 \times 10^{-6}$$

Hence, for thermocouple TC-1 equation (13) is arrived at:

$$\text{Deviation} = -0.07712 E_{st} + 1.334 \times 10^{-6} (E_{st})^2$$

Table 26 is now constructed. Values of t substituted in equation (11) yield corresponding values of E_{st} which are then used in equation (13) to find the respective deviations. Each deviation is applied to the proper E_{st} to evaluate E_{TC-1} .

TABLE 26

CALIBRATION TABLE FOR THERMOCOUPLE TC-1

$t^{\circ}\text{C}$	$E_{st} \text{ uv}$	Deviation uv	$E_{TC-1} \text{ uv}$
-28	1042.8	79.0	963.8
-30	1114.4		
-32	1185.3	89.5	1095.8
-34	1256.0		
-36	1326.1		

The second method ^{20,21} utilized in establishing a calibration

20. R. Wiehe and M. Brevoort, Rev. of Sci. Inst. 2, 450(1931)

21. Temperature: Its Measurement and Control in Science and Industry, Am. Inst. of Physics, Reinhold Publishing Co., N.Y. (1941) pp. 210-211

TABLE 1. Deviations of the observed values from the calculated values.

Deviation (m)	Deviation (m)	Deviation (m)
-107.3	112.1	122.3
-122.3	122.3	122.3

TABLE 2. Deviations of the observed values from the calculated values.

-107.3	-122.3
-122.3	-122.3

TABLE 3. Deviations of the observed values from the calculated values.

$$a = -0.0771$$

$$b = 1.124 \times 10^{-2}$$

TABLE 4. Deviations of the observed values from the calculated values.

$$a = -0.0771, b = 1.124 \times 10^{-2}$$

TABLE 5. Deviations of the observed values from the calculated values.

TABLE 6

TABLE 7. Deviations of the observed values from the calculated values.

Deviation (m)	Deviation (m)	Deviation (m)	Deviation (m)
107.3	112.1	122.3	122.3
122.3	122.3	122.3	122.3

TABLE 8. Deviations of the observed values from the calculated values.

TABLE 9. Deviations of the observed values from the calculated values.

table is a modification of the first. Whereas the first involves solving an equation such as (11) for values of E_{st} values from a calibration table²¹ for a standard Cu-constantan thermocouple, are used here.

The constants in equation (12) are evaluated and an equation (14) (see below) similar to (13) is obtained. E_{TC-1} values for corresponding temperatures are then calculated as before using equation (14) and the standard reference table²¹.

The calculations are summarized in the following paragraph: From the reference table in Temperature: Its Measurement and Control²¹ E_{st} values corresponding to T_{CO_2} and T_{Hg} are found.

T	E_{st}	E_{TC-1}	Deviation
(T_{Hg}) -38.87°C	1408.5 uv	1319.1 uv	-89.4 uv
(T_{Hg_2}) -78.37	2707.8	2515.9	-191.9

Solving simultaneous equations as before,

$$a = -0.067742$$

$$b = -0.03032 \times 10^{-4}$$

Substituting these values in equation (12),

$$\text{Deviation} = -0.067742 E_{st} - 0.03032 \times 10^{-4} (E_{st})^2 \quad (14)$$

Using equation (14) and the standard reference table²¹, the calibration table 27 is constructed:

TABLE 27
CALIBRATION TABLE FOR THERMOCOUPLE TC-1

T	E_{st}	Deviation	E_{TC-1}
-28°C	1040.3 uv	-73.8 uv	966.0uv
-30	1111.8	-79.1	1032.7
-32	1182.8	-84.3	1098.5
-34	1253.4	-89.7	1163.7
-36	1323.6	-95.0	1228.6

A theoretical consideration²² of thermocouples indicates that for most metals the values of the E.M.F.s in the couple circuit plotted against the temperatures of the varying junction results in a curve that is sensibly a parabola. The equation for this curve is given:

$$e = at + bt^2 \quad (15)$$

where a and b are constants and b is negative. Substituting in turn for t the values T_{CO_2} and T_{Hg} in centigrade degrees and for the e the corresponding E.M.F.s in microvolts, results in two simultaneous equations (16) and (17) which are solved for a and b.

$$2515.9 = -78.37 a + (-78.37)^2 \quad (16)$$

$$1319.1 = -38.87 a + (-38.87)^2 \quad (17)$$

thus,

$$a = -35.75$$

$$b = -0.04662$$

These values of a and b are inserted in (15) to obtain (18):

$$e = -35.75 t - 0.04662 t^2 \quad (18)$$

which is then utilized in setting up the third thermocouple calibration table shown here (Table 28)

TABLE 28
CALIBRATION TABLE FOR THERMOCOUPLE TC-1

t	E calculated
-28°C	964.4 uv
-30	1030.54
-32	1096.26
-34	1161.61
-36	1226.58
-38.78	1319.1 (observed)

22. Gilbert, N.E. Electricity and Magnetism, Macmillan Co. (41)

Below in table 29 is presented a summary of the three calibration tables calculated in the preceding paragraphs:

TABLE 29

A COMPARISON OF VALUES OF E_{TC-1} CALCULATED BY THREE METHODS

t	E_{TC-1}		
	Observed	Method 1	Method 2 Method 3
-28°C		963.8 uv	966.0 uv 964.4 uv
-30			1032.7 1030.54
-32		1095.8	1098.5 1096.26
-34			1163.7 1161.61
-36			1228.6 1226.58
-38.87	1319.1 uv		
-78.37	2515.9		

Inspection of the calculated values of E_{TC-1} will reveal the excellent agreement existing. The average difference in the temperatures corresponding for an observed E.M.F. calculated by the three methods is 0.07°C. Since method 3 yields values intermediate to those of the other two and in addition is more convenient it is adopted for use with the thermocouple TC-1.

A working calibration table for thermocouple TC-1 is constructed using equation(18) of method 3.

$$e = -35.75 t - 0.04662 t^2 \quad (18)$$

Table 30 is shown on the following page.

FIG. 19 HEATER CIRCUIT USED IN DETERMINATION OF CALORIMETER HEAT CAPACITY

TABLE 30
CALIBRATION TABLE FOR THERMOCOUPLE TC-1

$t^{\circ}\text{C}$	$E_{\text{TC-1}}$ uv	E uv	dE/dT uv/ $^{\circ}\text{C}$
-28	964.4	66.1	(-29°C) 33.05
-30	1030.54	65.72	(-31°C) 32.86
-32	1096.26	65.35	(-33°C) 32.68
-34	1161.61	64.97	(-35°C) 32.49
-36	1226.58		

or in greater detail, to afford convenience in use,

$t^{\circ}\text{C}$	$E_{\text{TC-1}}$ uv	dE/dT uv/ $^{\circ}\text{C}$
32.00	1096.26	32.77
32.25	1104.45	32.75
32.50	1112.64	32.72
32.75	1120.82	32.70
33.00	1128.98	32.68
33.25	1137.14	32.65
33.50	1145.30	32.63
33.75	1153.46	32.61
34.00	1161.61	32.59
34.25	1169.76	32.56
34.50	1177.90	32.54
34.75	1186.03	32.52
35.00	1194.16	32.49
35.25	1202.28	32.47

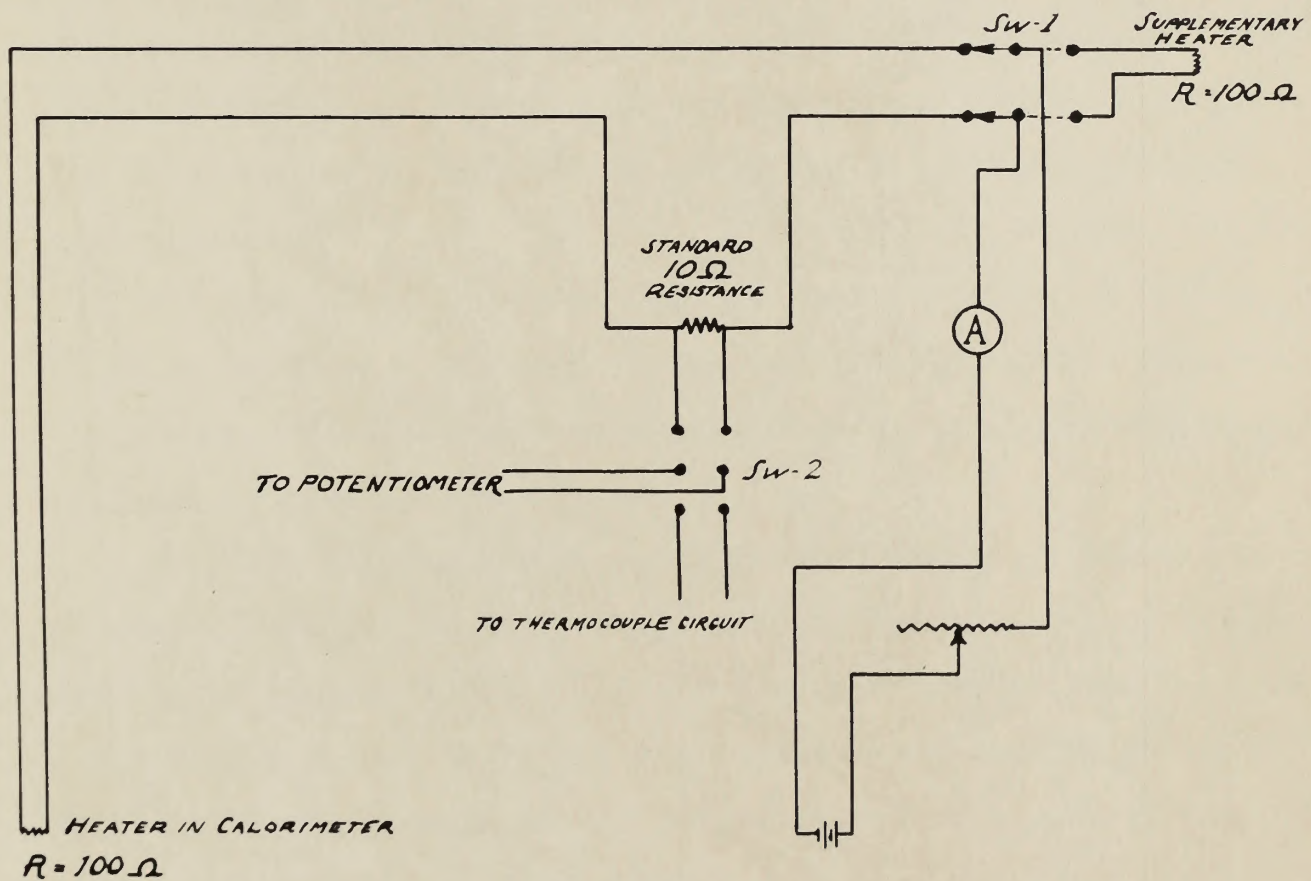
Interpolations are readily made to find values of dE/dT for average E.M.F.s or temperatures.

B. Determination of the heat capacity of the calorimeter.

The effective heat capacity of the calorimeter varies with the height of the liquid ammonia within the Dewar. The value of the heat capacity is utilized in calculating the heat effect (see calculations) of the reaction occurring in the calorimeter.

The procedure followed involves measuring the temperature rise produced in a weighed quantity of toluene in the calorimeter when a definite amount of heat from an electric heater is

FIG. 19 HEATER CIRCUIT USED IN DETERMINATION OF CALORIMETER HEAT CAPACITY



added to the toluene.

The major modifications of the calorimeter for determining the heat capacity consists of substitution of a 3 mm. diameter glass rod containing #32 cotton wound manganin leads, 82 centimeters in length to a coiled wire heater in the place of the sample-bulb rod assembly. The heater is 720 centimeters of #32 cotton wound manganin wire with a resistance of 98.5 ohms. The heater circuit is a standard 10 ohm resistance certified by Leeds and Northrup the voltage across which can be determined by the potentiometer.

The resistance of the manganin heater and leads as determined by means of a portable bridge is found to be 99.5 ohms

0.1 ohms. When the coil is immersed in toluene the resistance is found to have the same value.

Into the calorimeter is put a weighed amount of toluene (Eastman-Kodak 325 (Sulfur free)) redistilled to obtain fraction distilling between 109.5 - 110.5°C (uncorrected)(literature 110.8) a sufficient amount to fill the calorimeter to same height as does the liquid ammonia in the determination of a heat of reaction. The calorimeter is assembled with the heater and leads replacing the sample bulb.

It is advisable to attach a drying tube filled with a desiccant to the calorimeter outlet which is sealed to the gas-collecting system. The toluene is cooled to below the boiling point of liquid ammonia with dry ice and acetone bath and is then thermostated with liquid ammonia (cf to previous procedure).

added to the solution.

The major contribution of the calorimeter for determining

the heat of solution of a substance is the heat of solution

of a substance in a solvent. The heat of solution of a substance

is defined as the heat of solution of a substance in a solvent

at a constant pressure. The heat of solution of a substance

is defined as the heat of solution of a substance in a solvent

at a constant pressure. The heat of solution of a substance

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at a constant pressure. The heat of solution of a substance

is defined as the heat of solution of a substance in a solvent

at a constant pressure.

It is advisable to obtain a value for the heat of solution

of a substance in a solvent at a constant pressure. The heat

of solution of a substance in a solvent at a constant pressure

is defined as the heat of solution of a substance in a solvent

at a constant pressure. The heat of solution of a substance

The temperature drift is then observed at one minute intervals. For each filling of the calorimeter to any one height, three heating periods are conducted, one below -33° , one at -33° and one above. The times of closing and opening the heater circuit are tabulated. During the heating process, the E.M.F. across the 10 ohm standard resistance is measured by the potentiometer. A double pole-double throw switch expedited switching the potentiometer from the thermocouple circuit to the circuit through the standard resistance. The requirement of a steady current flow through the heater is met by allowing the batteries that supply heater current to discharge continuously for several hours beforehand. For this reason an auxiliary 100 ohm heater coil is provided which is switched into or out of the circuit by a double pole-double throw switch.

The temperature change associated with each period of heating is evaluated from the E.M.F. curves in similar fashion as previously described¹³ under calculations of heat of reaction.

The total heat input during any heating period is found by equation (19):

$$q = \frac{I^2 R t}{4.1833} \quad (19)$$

where q is the total heat input in calories corrected for the heat developed in the leads. I is the mean current in amperes, and t is the time of the heating period in seconds. The heat developed in the leads is calculated by assuming R to be $\frac{1}{2}$ the total resistance of both leads. The total heat input, q , produces the observed temperature rise, ΔT_{obs} , in the calorimeter

and contents of heat capacity $C_{p, \text{toluene}}$ and $C_{p, \text{toluene}}$ respectively. The value of $C_{p, \text{toluene}}$ is calculated from the specific heat of toluene at -35°C and the weight of toluene present. Then the value $C_{p, \text{calorimeter}}$ is calculated from equation (20):

$$(20) \quad C_{p, \text{cal}} = \frac{Q}{\Delta T_{\text{obs}}} - C_{p, \text{toluene}}$$

The values of $C_{p, \text{cal}}$ are then plotted against calorimeter

liquid levels.

The values of the heat capacity as a function of liquid

level determined by the preceding method are found to differ considerably from values obtained in previous work for the same calorimeter by three other methods. (See Table 31)

The first of these three earlier methods, a method similar to that just described using toluene, utilized a weighed quantity of water at 25°C in the calorimeter rather than the toluene. An insulated heater supplied the heat input. Resulting heat capacities varied almost linearly with liquid level as Figure 30 illustrates were obtained from the calculated heat capacities for 25°C by extrapolating to -35°C . The values are somewhat high compared to those of all other methods.

The second earlier method involved vaporization of an amount of ammonia from the calorimeter into the gas-collecting system, observing the accompanying temperature change brought about in the calorimeter by the removal of heat in the vaporization process.

The first of the earlier methods consisted of bubbling hydro-
gen gas from a gas burst through the ammonia in the calorimeter.

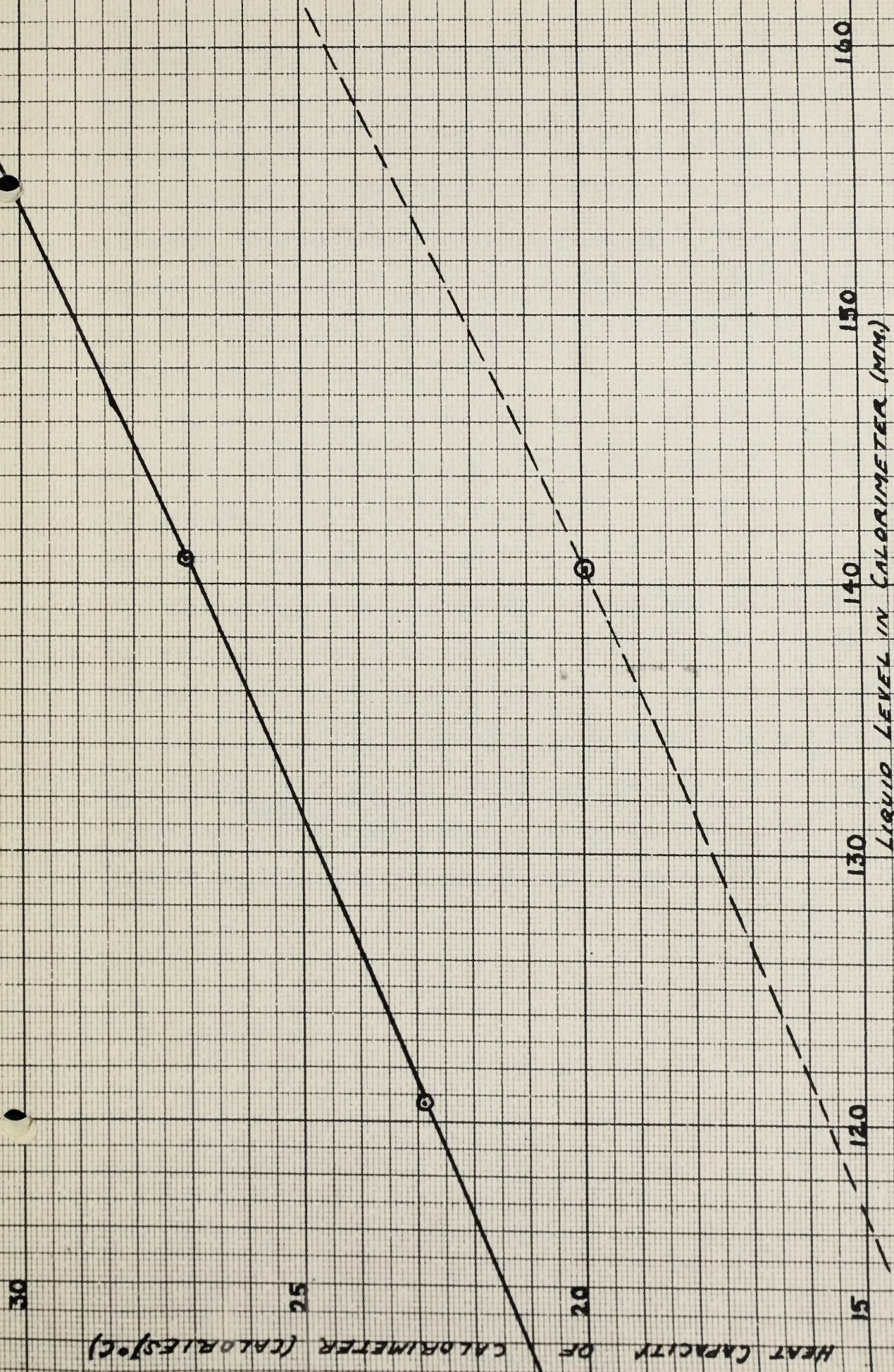


FIG. 20 HEAT CAPACITY OF CALORIMETER

— CURVE OF WATER METHOD OF CALIBRATION.

--- CURVE DRAWN PARALLEL TO UPPER CURVE THROUGH SINGLE NH_3 -VAPORIZATION METHOD OF CALIBRATION VALUE.

collecting the hydrogen and vaporized ammonia and observing the temperature change of the calorimeter. The heat capacity thus determined agreed fairly well with that determined by the preceding method, as can be seen by reference to table 31. Unfortunately, this hydrogen-bubbling experiment was not carried through with complete accuracy but was performed to check the order of magnitude of the heat value obtained by the method of vaporization of ammonia.

The vaporization of ammonia method then is considered to give the most reliable value of the heat capacity for this method most closely parallels the conditions that obtain in the determination of the heats of reaction.

The complete heat capacity curve (figure 20) obtained from the results of the water method (table 31) is transposed with respect to the heat capacity axis of the graph to pass through the one value of the heat capacity determined by the ammonia vaporization method. Values of heat capacity for corresponding liquid levels from this transposed curve (figure 20) are used in the calculations throughout this research.

collecting the hydrogen and vaporized ammonia and observing the
 temperature change of the calorimeter. The heat capacity thus
 determined agreed fairly well with that determined by the gas-
 expansion method, as can be seen by reference to Table 31. Unfor-
 tunately, this hydrogen-ammonia experiment was not carried
 through with complete accuracy but was performed to check the
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 the results of the water method (Table 31) is transposed with
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 the one value of the heat capacity determined by the ammonia
 vaporization method. Values of heat capacity for corresponding
 liquid levels from the transposed curve (Figure 20) are used
 in the calculations throughout this research.

TABLE 31

A SUMMARY OF CALORIMETER HEAT CAPACITY
DETERMINATIONS

Liquid Height mm.	Heat Capacity cal/°C		
	Water Method (24°C)	Toluene Method	NH ₃ Vaporization
120.7	25.3 **		
122.0		9.2	
139.3		12.7	
140.5			20.9 *
140.9	30.0 **		
158.4	34.6 **		

* Hydrogen-bubbling experiment confirmed this order of magnitude. (19.0 cal/°C)

** These are values obtained by interpolation of the data from 24° C to - 33° C.

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